University of Cincinnati

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I, Meixi Zhang , hereby submit this original work as part of the requirements for the degree of Master of Science in Materials Science.

It is entitled:

Synthesis, characterization of graphene and the application of graphene carbon nanotube composite in fabricating electrodes

Student's name: **Meixi Zhang**

This work and its defense approved by:

Committee chair: Vesselin Shanov, Ph.D.

Committee member: Mark Schulz, Ph.D.

Committee member: Donglu Shi, Ph.D.

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Synthesis, characterization of grapheme and the application of grapheme carbon nanotube composite in fabricating electrodes

A thesis submitted to the Graduate School

Of the University of Cincinnati in partial fulfillment of the requirements for the degree of

Master of Science

In the Department of Mechanical and Materials Engineering

College of Engineering and Applied Science

By

Meixi Zhang

B.A. Heilongjiang University, June 2011

Committee Chair: Vesselin Shanov, Ph.D.

Abstract

This thesis discussed chemical vapor deposition synthesis of graphene and the characterization technique on graphene. The work was mostly concentrate on discovering varies catalysts and modifying optimized recipes for each catalyst. The research was consisted of the following parts: (1) study on nickel catalyst for growing graphene; (2) exploring the role of gadolinium on graphene synthesized on nickel catalyst; (3) study on copper catalyst for growing graphene on Black Magic; (4) characterization of graphene using different techniques; (5) synthesis of graphene and carbon nanotube hybrid and its application on electrodes.

A series of experiments were conducted and optimized recipes were obtained for different catalysts including a reproducible recipe for a new model of CVD facility called Black Magic; Raman Spectroscopy, Scanning Electron Microscope, Transmission Electron Microscope and Gamry Instrument were used to characterize graphene as well as graphene andesertation format
d CNT arrays composite.

There was enough data to draw the conclusion of successful synthesis of graphene on nickel, copper and a new discovery of the role of gadolinium in CVD synthesis of graphene was obtained. A new structure of graphene and CNT arrays composite was synthesized and the application of this structure in electrodes application was achieved.

Acknowledgements

I would like to extend my gratitude to all the people who helped to bring this thesis project to fruition. First, I would like to thank Dr. Vesselin Shanov for providing me the opportunity of joining Nanoworld and stating the project on graphene. I am so deeply grateful for his help, professionalism, valuable guidance and financial support throughout this project and through my entire program of study.

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Table of Contents

1. Introduction:

1.1 Organization of the thesis

Graphene, a one atom thick sheet of carbon atoms densely packed into honeycomb structure, has attracted scientists interests since the discovery of it by the two winners Andre Geim and Konstantin Novoselov, of 2010 Noble Prize in physics. Emerging applications of graphene appear in both industry and science areas owing to its excellent properties in terms of electrical, thermal, mechanical properties and etc. Even though the researches about graphene have been boomingly developing, there is still a long way to go in order to develop mass production technique of graphene with good quality in industry.

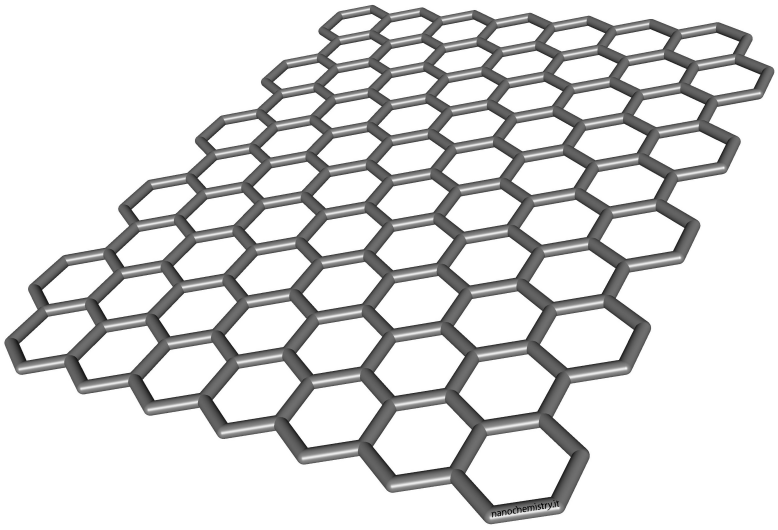


Figure 1 Schematic of graphene structure

In this thesis work, a brief introduction to graphene including the synthesis method, properties of graphene are discussed in Chapter 1. Chapter 2 emphasizes on the technique of Chemical Vapor Deposition (CVD) as the synthesis method of for

graphene and characterization techniques after grown. The experiment session mainly focuses on the CVD synthesis of graphene using nickel and copper catalyst. A novel hybrid structure of graphene and CNT and its application are also brought up in the experiment session. A brief review of the booming applications of graphene is introduced in the experimental session. The conclusion of this work will cover the summary of the thesis work and some perspectives on the future work.

1.2 Synthesis methods of graphene: top-down and bottom-up

Basically, the fabrication techniques at nano-level can be broken down to two main categories: top-down and bottom-up.

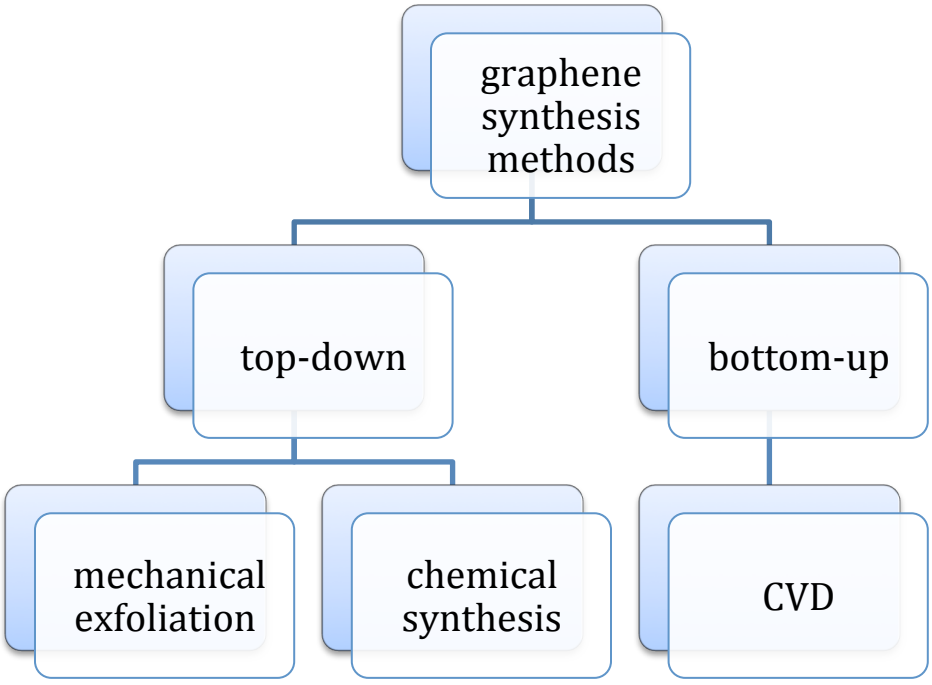


Figure 2 The schematic of difference methods of synthesizing graphene

The commonly adopted synthesizing methods of graphene that will be discussed in this thesis work are listed Figure 2.

1.2.1 Mechanical exfoliation

Mechanical exfoliation is the first recognized technique to synthesize graphene, which is a top-down technique. It works in such a way that a longitudinal and transverse stress is applied or generated on the surface of a layered structure material using simply a scotch tape or an AFM tip to slice one or a few layers from the material and place them on a target substrate. It was first reported by [1]that they used mechanical exfoliation technique of oxygen plasma etching assisted with further AFT tip manipulation to obtain very thin highly oriented pyrolytic graphite (HOPG) section that went down to ~200nm, which was approximately 600~700 layers of graphene single sheets.

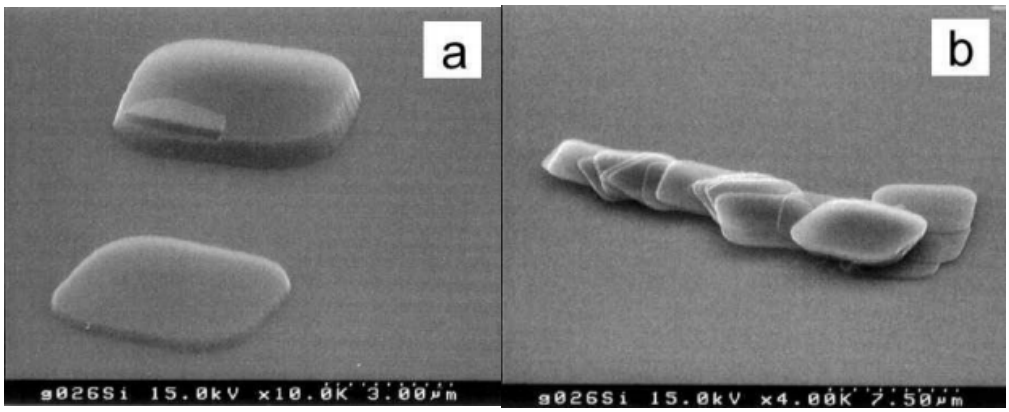


Figure 3 SEM images of graphite plates on the Si (001) substrate. [1]

Later on, the two Russian scientists who were awarded for 2010 Nobel Prize in physics because of the discovery of single layer graphene first published their results in 2004.[2] They started with 1-mm-thick platelets of HOPG for dry etching in oxygen plasma using 5 microns deep mesas on top of the platelets. Then they

pressed the prepared substrate against a 1-μm-thick layer of a fresh wet photoresist spun over a glass substrate, followed by heating to enhance the adhesion between the HOPG mesas and the photoresist layer. A scotch tape was then used to repeatedly peel flakes of graphite off the mesas, and the flakes were released in acetone. The thin flakes were then collected with n-doped Si wafer with a SiO_2 layer on top followed by ultrasound cleaning in propanol to remove thick flakes. After all the procedures, thin flakes (d<10nm) were found to attach strongly to SiO_2 due to van de waals and/or capillary forces.

The mechanical exfoliated graphene has been applied into the field of application of transistors, which has boomed the interests of researchers and scientists to focus on a new generation of electronic devices based on graphene.

However, there are still limitations of using mechanical exfoliation method to fabricate graphene: graphene with defects and low purity is always obtained from such a method. Hence, the improvements in industry mass production of defect-free, high purify and controllable-layered graphene is an issue needs to be further studied.

1.2.2 Chemical synthesis

There is another top-down technique of synthesizing graphene named chemical exfoliation, which is a process by which alkali metals are intercalated with the graphite structure to isolate few-layer graphene dispersed in solution. Alkali metals have this advantage that they are smaller than the interlayer spacing of graphite, so they can easily fit in the interlayers as shown in figure 4. [3] Graphite is

intercalated with potassium metal to form the first stage compound KC_8. Exfoliation in ethanol produces potassium ethoxide and hydrogen gas that will aid in separating the graphitic sheets to form graphite nanoplatelets.

This methods has advantage in terms of industry mass production due to its low cost solution-phase method, it can be easily scaled up and could be a method to produce graphene-based composites, by which additives could be mixed with graphene at the liquid phase.

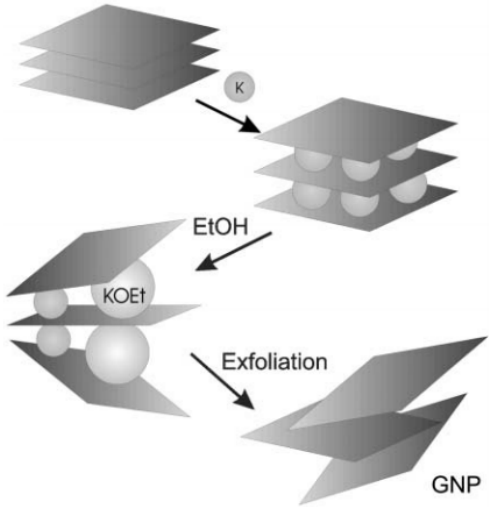


Figure 4 Schematic diagram showing the intercalation and exfoliation process to produce graphite nanoplatelets (GNP). [3]

Fabricate graphene by reducing graphite/graphene oxide (RGO) is currently one of the most commonly adopted methods to synthesize graphene for many applications, especially for energy storage application such as, super-capacitors and batteries. This is a chemical synthesis method by reducing graphite/graphene oxide to graphene using reducing agent. It has been acknowledged from one of the inventors Andre Geim that Boehm, et al was the first to demonstrate single layer of graphene

flake from reduced graphite oxide in 1962. They took the route of dispersing the oxide graphite flakes yielded from oxidation of graphite, and then reduced them back to graphene. There are three popular methods available for GO synthesis: the Brodie method (Brodie. 1860), Staudenmaier method (Staudenmaier. 1898) and Hummers and Offeman methods (Hummers and Offeman. 1958). All three methods involve oxidation of graphite using strong acids and oxidants.[4]

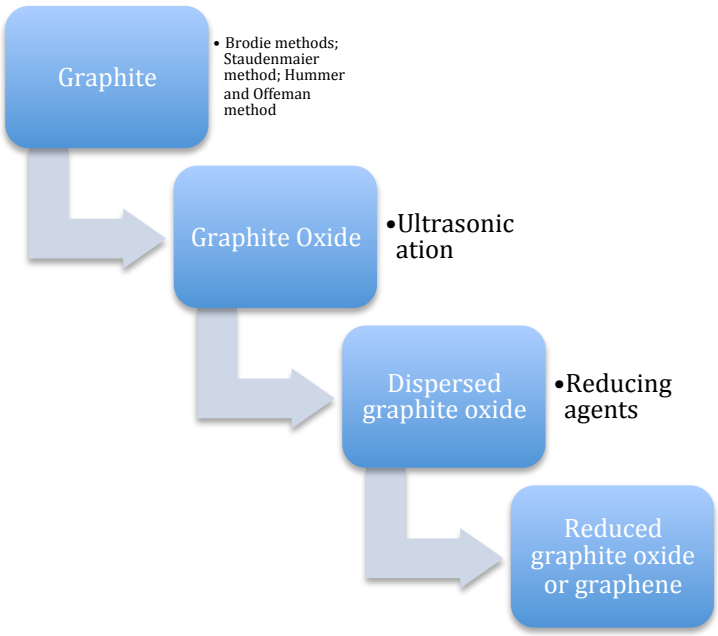


Figure 5 The process flow chart of graphene derived from reduced graphite oxide

The process flow chart of graphene synthesis derived from reduced graphite oxide is shown in Figure 5. The general procedures of the chemical synthesis of graphene using this method are interpreted as the following: oxidize graphite to GO by Hummers method (mostly commonly adopted now), which is mixing graphite with sodium nitrite, sulfuric acid and potassium permanganate; the interlayer spacing of will increase to two or three times larger than pristine graphite after oxidization and sonication; therefore there will be single or a few-layer flakes suspend in

solution; by applying reducing agents such as hydrazine hydrate, suspended GO reduces to graphene.

There are flood developments of this chemical synthesis method after 2006, when Ruoff and his coworkers produced mono-atomic graphene by a chemical synthesis process.[5, 6] Now the ROG method has been one of the most popular methods of synthesizing graphene especially in terms of the energy storage applications. The specific surface area that can be obtained by using this method goes up to 3523 m^2/g [7] with a porous 3-D graphene structure. There are booming researches in RGO by either chemical reduction or thermal reduction of GO to synthesize graphene. [8-11]

However, for the chemical synthesis of graphene by reducing GO, the concerns for this method are that there are defects introduced to graphene and the mechanical strength of graphene prepared in such way is low. In the energy storage related applications of graphene, RGO would be an excellent candidate due to the defects where other additives such as metal oxides, polymers can be mixed in with graphene to improve the capacitance.

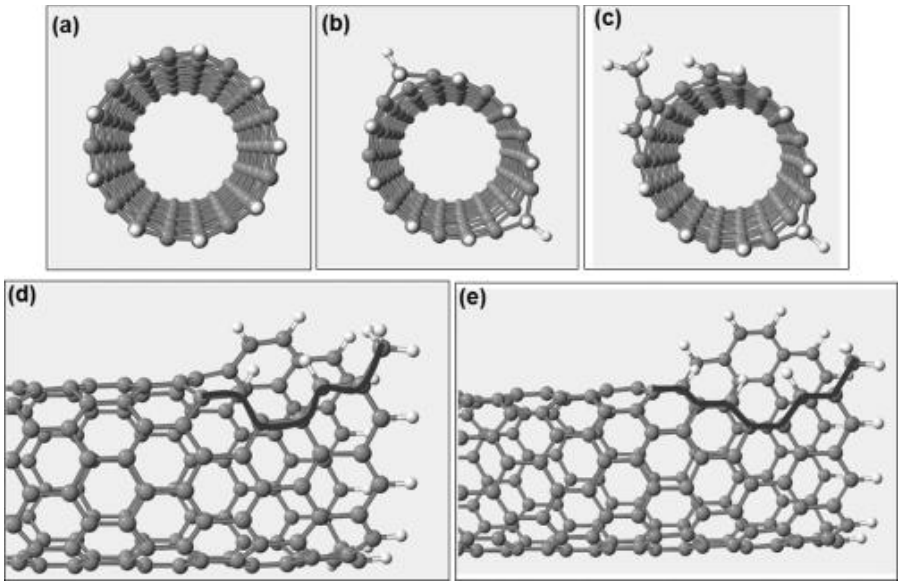


Figure 6 Unzipping CNT to obtain graphene nano-ribbons. Permission obtained from [12]

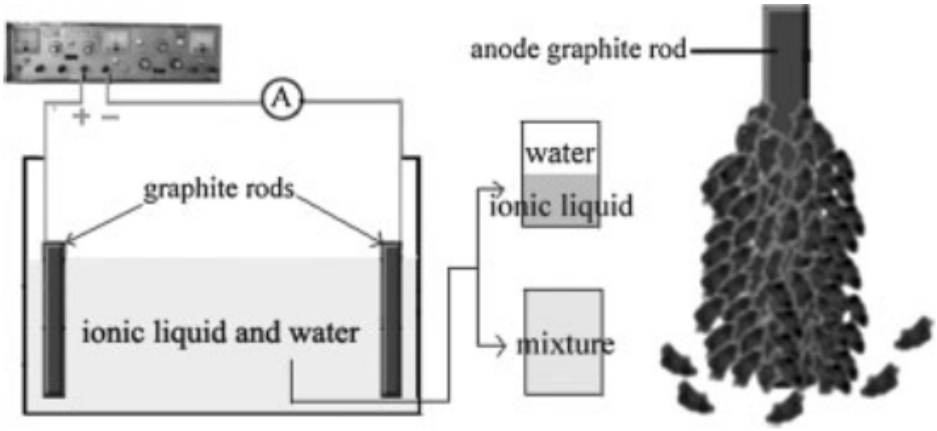


Figure 7 Electrochemical exfoliation of graphene. Permission obtained from [13]

Besides the methods of mechanical exfoliation, chemical exfoliation, chemical synthesis and CVD of graphene, there are also other unique means to fabricate graphene like, unzipping carbon nanotubes[12] and electrochemical synthesis.[13] All the techniques have been highly acclaimed by the researchers in their respective fields regarding respective application directions. However, there are still ongoing researches about large area, defect-free mass production of graphene with reproducibility; this is a robust area that will attract more attention as it develops.

1.3 Properties of graphene

There are a lot of researches about graphene in terms of its outstanding properties in electrical conductivity, thermal conductivity, mechanical strength, the transparency, etc. The basic electrical, thermal and mechanical properties will be discussed here.

A single carbon atom has four valence electrons with a ground state electronic shell configuration of He $2s^2p^2$. In the case of graphene, there are three hybridized orbitals around each carbon atom, which are s, p, p. And each carbon atom is connected to three other carbon atoms in the honeycomb lattice and they are most responsible for most of the binding energy and for the elastic properties of graphene sheet. This is the most energetic stable structure with the sp^2 bonds composite graphene sheet, and graphene is thus a 2-dimentioan structure due to the fact that the geometry of sp^2 bonds are planar triangular.[4]

It is demonstrated that the band structure of graphene obtained from such a tightly biding model, which yields symmetric conduction and valence bands with respect to the Fermi energy se at 0eV. This is the reason why graphene is called a 0 bad-gap semiconductor.

Experimental results from transport measurements show that graphene has remarkably high electron mobility at room temperature, with reported values higher than 15,000 $cm2 \cdot V^{-1} \cdot s^{-1}$.[14] The corresponding resistivity of the graphene sheet would be 10−6 Ω·cm. This is less than the resistivity of silver, the lowest known at room temperature.[15]

Owing to the excellent electric properties, graphene has been adopted in many related application fields, for example, the research of replacing silicon with graphene in semiconductor fabrication; graphene stepping in for solar cells manufacture taking place of ITO and so on.

Graphene is one of the strongest materials that's ever known with fracture strength over 100 times greater than a hypothetical steel film of the same (thin) thickness with the Young's Modulus of 1 TPa (150,000,000 psi).[16] The Nobel announcement stated this by saying that a 1 square meter graphene hammock would support a 4 kg cat but would weigh only as much as one of the cat's whiskers, at 0.77 mg (about 0.001% of the weight of 1 m^2 of paper).[17] There are researches of mixing graphene with polymers to enhance the mechanical properties of the materials taking advantage from the high mechanical strength of graphene. It would be ideal if graphene and the additives can be uniformly mixed either by physical contact or the chemical bonds.

Graphene is a perfect thermal conductor, too. The in-plane thermal conductivity of graphene at room temperature is among the highest of any known material, about 2000–4000 W m^{-1} K^{-1} for freely suspended samples.[18] In the applications such as the fabrications of integrated electric circuits, fast heat dispassion from a graphene layer could be expected to increase the efficiency and life span of such a device due to reduced heat damage.

2. CVD synthesis and characterization of graphene

2.1 Chemical Vapor Deposition.

Chemical vapor deposition is a synthesis process where the chemical ingredients react in the vapor phase near or on a heated substrate to form a solid deposit. Normally, CVD process involves flowing a precursor gas or gases into a heated chamber containing one or more solid substrates for depositing a thin layer of solid film. Chemical reactions occur near or at the hot surface of the substrates, resulting in the deposition of a coating on such substrates. This process is accompanied by the production of one or more by-products that are exhausted out the system along with the untreated precursors. CVD is practiced in a variety of formats, as categorized by the means of conducting the experiments it can be classified into atmosphere pressure CVD (APCVD), low pressure CVD (LPCVD) and plasma-enhanced CVD (PECVD).

CVD has a lot of advantages regarding the coating technique. One of the advantages is that the deposition of the coating via CVD is uniform regardless of the shapes of the substrates, i.e. the thickness of the deposition on the sidewalls will be the same as on the top surface of the substrate. This is a major advantage when coating elaborately designed substrate comparing with some of the traditional deposition techniques like physical vapor deposition such as sputtering and e-beam deposition.

Another advantage of CVD is that it can be used to deposit with really high purity, this is owing to the process of purification of the precursors that removes all the

impurities. Other than that, CVD also has the advantages of high deposition rate, and the fact that it doesn't require a high vacuum environment as PVD does, which saves the expense and labor on maintaining a critical vacuum condition.

Even though CVD beats over PVD in some aspect, it still has some disadvantages. A major one is that it requires a precursor that volatiles at near room temperature, although there are some metal-organic precursors that helped ease the problem, there are still limitations when it comes to the non-replaceable precursors. Moreover, the precursors can be toxic, explosive and corrosive. For example, the mixture of gases foe synthesizing graphene consists with methane, hydrogen and argon. Last but not the least, CVD is almost always conducted at elevated temperatures due to the high decomposition temperature of the precursors. This fact puts some limitations on the kinds of substrates that can be used, which have to have the capability to stand relatively high temperature. It also restricts the possibilities of using bi-substrate consists different thermal expansion co-efficiencies in some cases. [19]

CVD is commonly used in depositing thin layers of coating that the traditional methods are not capable of. There are a number of applications of CVD, among which there are some critical industry sectors. Coating is one of the most important application areas that CVD can be utilized to coat a variety of products for wear resistance, corrosion resistance, high temperature protection, erosion resistance and combinations thereof. Semiconductors and related devices such as integrated circuits, sensors and optoelectronic devices are another critical application of CVD. There are some ceramic matrix composites that are produced from CVD including

carbon-carbon, carbon-silicon carbide composites; this process is sometimes called chemical vapor infiltration or CVI.

2.2 CVD synthesis of graphene

The fabrication techniques of graphene like mechanical exfoliation, chemical exfoliation, chemical synthesis, reduce graphite oxide, unzipping CNTs and electrochemical exfoliation have been introduced in previous chapter. CVD synthesis of graphene will be the main topic for this chapter.

CVD is one of the best synthesizing method for graphene in terms of yielding high purity and defect-free graphene. Usually, a catalyst of transient metal is used in CVD synthesis. The mechanism of CVD synthesizing graphene using transient metal is generally a two-step mechanism. The first step is known as the dilution or incorporation of graphene in transient metal, where carbon atoms are absorbed and adsorbed in the metal with difference in the level of absorption and adsorption due to the difference in the solubility of carob atoms in difference metals. Following that, the second step takes place when cooling the whole system down to room temperature where the absorbed carbon atoms start to bond with each other and format the hexagonal ring of graphene flakes.[20] it is also possible by using CVD synthesis of graphene, the size of the graphene flakes can be controlled as of the state-of-art that the dimension reaches millimeter size. CVD synthesis of graphene consists of several steps that are: a temperature ramp step that is usually conducted under an inert environment with argon/helium purge, hydrogen can be added in

some cases in order to prevent the substrates from oxidizing in some cases that the substrates are with low purity; an annealing step is running under a certain high temperature where all the impurities are removed and grain size of the substrates is enlarged in the cases where transient metals such as nickel and copper are used; the actual growing step where the precursor with carbon source is introduced that it will decomposed to carbon atoms that will deposit on the substrates to build the honeycomb structure; and then the last step to cool the whole system down from high temperature to room temperature, where a relatively fast cooling rate is needed in order to yield graphene with good quality.

The CVD synthesis of graphene can be categorized into two main categories: atmosphere pressure CVD and low pressure CVD. The growing kinetics is difference under the two different modes, and the recipe also varies regarding the different catalysts being used.

Being synthesized under difference pressure, the kinetics of the formation of graphene flakes can vary resulting in difference shapes, sizes and uniformity[21], for instance, a lope-shape graphene domain can form in LPCVD[22], while a hexagonal-shape graphene domain form in APCVD[23].

Other than pressure, there are a number of parameters that have influence on the formation of graphene. Namely, temperature, gas ratios, and the different catalysts all play crucial roles. There have been extensive researches in modifying the recipes of CVD graphene synthesis. The lowest temperature that has ever been reported so far is 240°C, plasma-enhanced CVD was adopted in this method[24]. The plasma and

metal coupling cause localized heating of the substrate that reduces the heating time. In addition, plasma has the ability to remove the impurities, such as the native oxide metal layer to guarantee the uniformity of the nucleation of graphene. [25]. However, there are disadvantages in PECVD, which include that continuous plasma damages the quality of graphene flakes by introducing defects in graphene due to the high energy pulse and it also causes the incoherence of graphene flakes on the metal substrates. In this regard, Woo et al. had reviewed that the quality of graphene is better under high temperature than under low temperature PECVD [26].

The ratio of the gases mixed together also interference with the result of graphene synthesis. There is a controversial on the concentration of hydrogen. There are some scientists believe that the presence of hydrogen degraded the crystallinity of graphene and slows down the growth rate of graphene on copper[27]. Hydrogen decomposes and chemisorbed in metal substrate, which competes with the dehydrogenation of hydrocarbon by occupying the surface actives sites, obstructing the growth of graphene as well as creating defect spots in graphene. [28] However, there are different opinions on this subject, some scientists hold the view that the presence of hydrogen is important for growing highly organized, uniform graphene. They believe that hydrogen keeps surface-bond carbon active in the meanwhile, etches away the unorganized carbons on graphene edges that will inhibit the formation of graphene hexagonal structure. It is reported by Vlassiouk et al [29]. That the growth of graphene can not happen without hydrogen being presence. High partial pressure of hydrogen is beneficial of the formation of CH_3 radicals, which is essential in growing graphene. Hydrogen here also works as a cleaner of the

unstable carbons on the edge of the hexagonal rings of graphene. Low partial pressure of hydrogen results in irregular spots of graphene. Regarding the issue of hydrogen competing with carbon species for the seats on metal surface, hydrogen has a much lower solubility in nickel, for example, than carbon, the fast recombination and desorption of hydrogen will always keep the surface of metal available for hydrocarbon and species[28].

There are varies transient metals can be used as the catalyst of CVD graphene. The most commonly adopted metals are nickel and copper. There are also a significant amount of researches on other metals such as iron, cobalt and so on, owing to their satisfying performance in CVD synthesis of carbon nanotubes. However, in this thesis work, only nickel and copper will be discussed for they are related to the experimental section.

2.2.1 Ni catalyst

Nickel is one of the most studied transient metals as the catalyst for CVD synthesis of graphene so far, though there is still not an agreed mechanism of how nickel works in the synthesis. The solubility of carbon in nickel is much higher than it in copper, which is 0.9% in weight at 900 °C as recorded[30], this fact gives an explanation why nickel tend to be the desired catalyst for synthesizing multi-layer graphene.

Due to the high performance of nickel as catalyst in synthesizing graphene via CVD, extensive researches have been carried out to study the mechanism of graphene growing on Ni (111) by modeling. It is proposed that the chain configurations are

the preferred thermodynamically over rings and present a high mobility (with long chains diffusing even faster than adatoms), whereas branched configurations are much less mobile but kinetically robust because they show substantial energy barriers for interconversion into other species [31]. L. Meng et al. [32] studied the influence of hydrocarbon concentration and temperature on the kinetics of graphene growing on Ni (111) surface using a classical molecular dynamics approach indicating that: low carbon concentration leads to disorder surface that is not favorable for sp^2 bonded graphene growing, results from the dissolution of carbon atoms into nickel and part of nickel atoms are kicked out of the surface; however, high concentration of carbon produces coordinated carbon instead of orderly sp^2 bonded graphene. The healing procedure, which is also called annealing is also investigated; showing the optimized temperature for growing graphene on nickel is at 1000 °C, where the quality of graphene is the best.

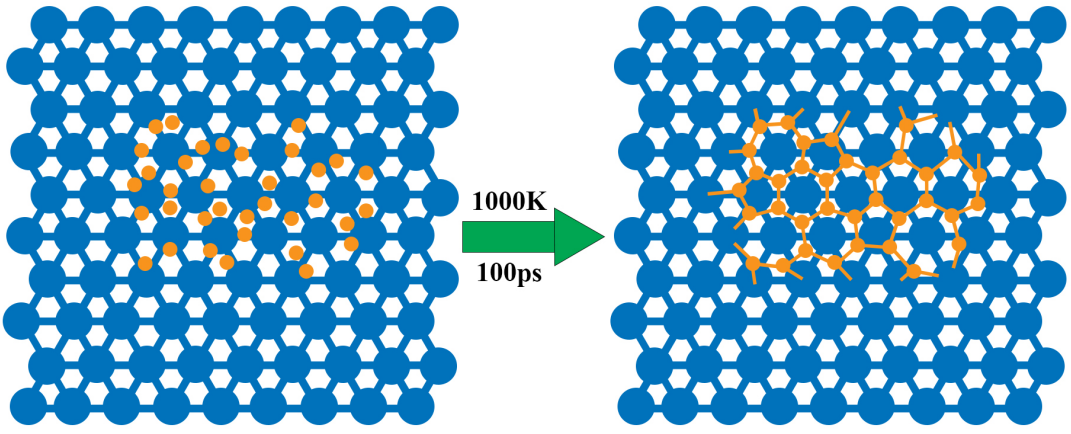


Figure 8 Modeling of CVD synthesis of graphene on Ni [32]

Polycrystalline nickel is also used as the catalyst of CVD synthesizing graphene due to the high performance it possesses. However, multi-layer and un-uniformity are

always found on graphene growing on nickel foil [20, 28, 33, 34]. Polycrystalline nickel has a large density of grain boundaries that contains a large number of lattice steps, where multi-layer graphene nucleates. Graphene flakes prefer to accumulate along the curvature of the grain edge, which leads to the formation of multi-layer graphene. It is reported that decreasing growing temperature to self-limit graphene segregation can reduce the solubility of carbon on nickel, but not to low that forms nickel carbide.[35] The high solubility and high carbon diffusion rate can be an advantage in controlling the number of layers. Xu et al. has proposed a method of synthesizing graphene by carbon diffusion on a nickel film.[36]

Extensive researches haven been done on CVD synthesizing graphene, yet there is still room to improve the subtleness in controlling the exact number of layer forming on nickel.

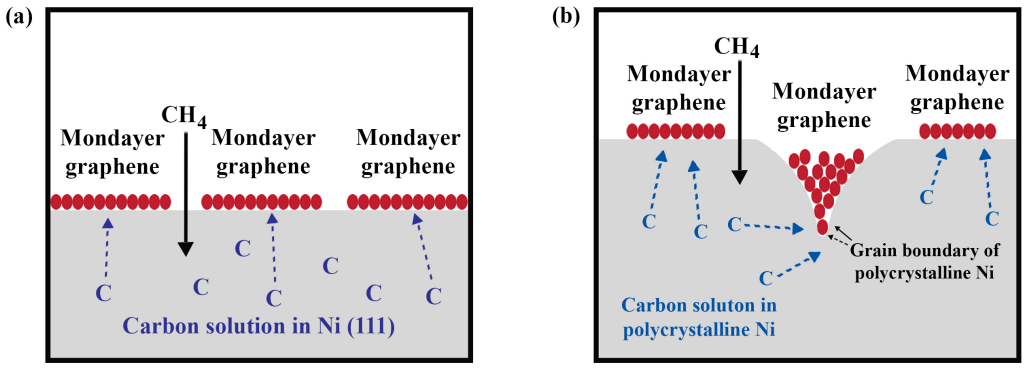


Figure 9 Graphene formation on (a)a single-crystal Ni (111) surface and (b) a polycrystalline Ni surface[37]

2.2.2 Cu catalyst

Copper has a different mechanism in working as the catalyst of synthesizing graphene compared to nickel. There also have been extensive studies on graphene growing on copper, where Ruoff's group has published several papers on studying the mechanism and kinetics by using isotopic labeling of carbon [23, 35, 38]. It is proposed that the growth of graphene on copper is surfaced mediate and limited diffusion of carbon into copper bulk occurred due to the low solubility of carbon on bulk copper[39]. There are different shapes of graphene islands formed on copper catalyst, for instance, dendritic shape[40-42] , hexagonal shape[22, 43-46] and four lobe flower shape[47, 48] on respective format of catalysts. The hexagonal shape of graphene islands is the desired shape of graphene forming on copper surface [22]. However, there is still no agreement on the mechanisms of varies shapes of graphene. Theory like, graphene islands undergo complex nucleation and simultaneously form graphene islands with multiple orientations; the four lobes flower shape would form when the growing speed is faster on the four corners[49] is accepted by some researchers while other theories are still under studying.

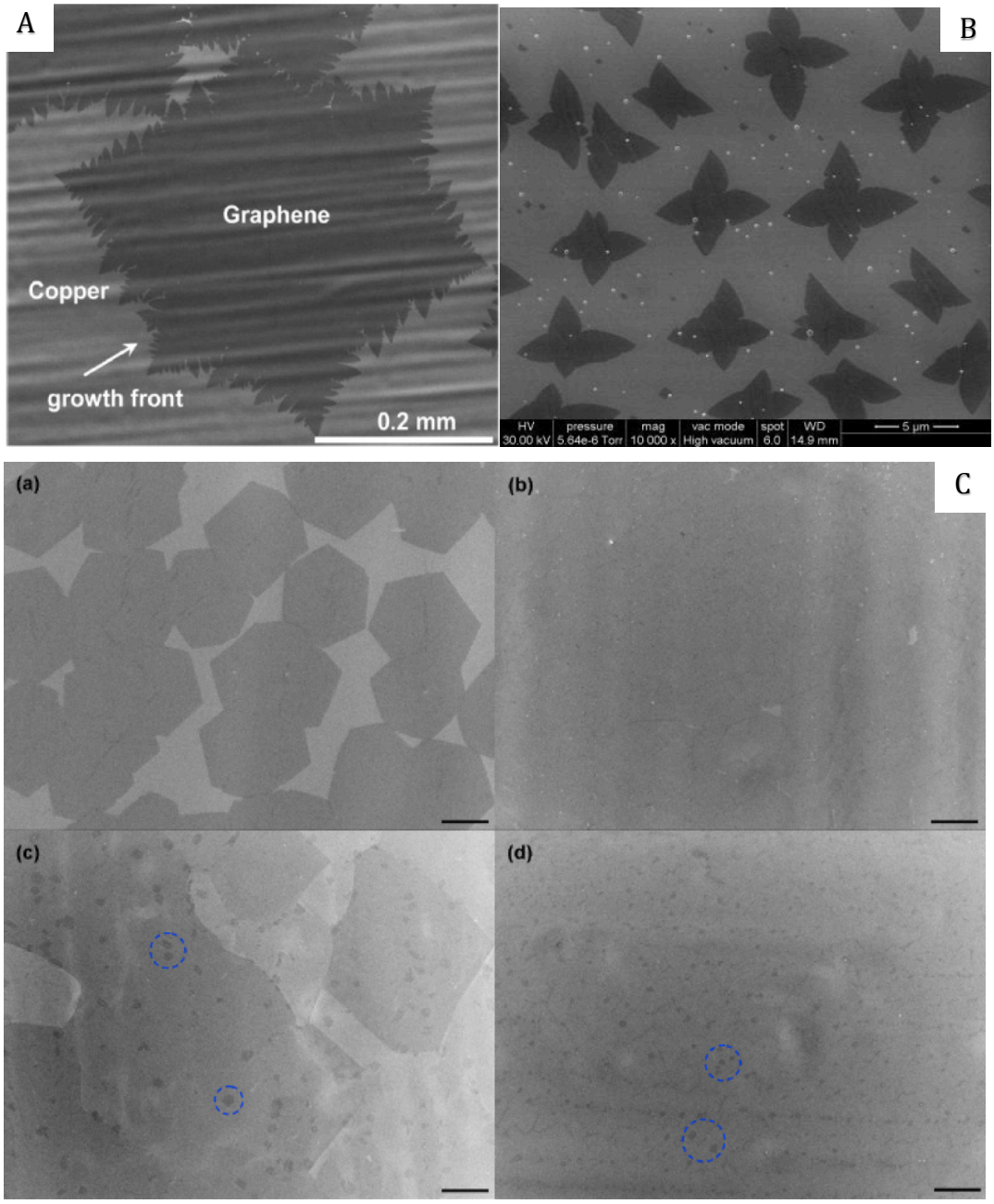


Figure 10 Different shapes of graphene islands. (A) dendrite shape[40], (B) four lobe flower shape. Permission obtained from [47], (C) hexagonal shape, visualizations of graphene flakes with different magnifications in (a), (b), (c), (d). [46].

Singly crystalline copper is used with different crystal facets to grow graphene, with the proof that only the facets of Cu (1 0 0) and Cu (1 1 1) [50] have chances on

yielding single-layer graphene, and multi-layer graphene will form on Cu (0 0 1) [51]. Nevertheless, polycrystalline copper foil is desired considering the expense on obtaining the catalyst compared with single crystal copper catalyst, since the catalyst will end up being sacrificed when trying to obtain pristine graphene on target substrate. The most commonly used temperature is 1000°C, but ranging from 800°C to 950°C on copper foil.

There are tremendous researches on CVD synthesis of graphene on copper and some of which are listed in the table below.

Table 1 Summary of the conditions of CVD copper graphene reported in the literatures

Pressure (Torr)	Annealing	Growth (H_2/CH_4)	Temperature °C	Cu catalyst	No. of layers	Reference
0.5	1000°C H_2 (2sccm, 0.04 Torr 30min)	0.06 1-60min growing; cooling: 40-300°C/min	1000	25μm	1	[47]
17	H_2 2sccm	1.5-4 90min	1035	25 (Cu foil enclosure)	1	[38]
0.46	90mTorr H_2 8sccm 30 mi	0.333, 30 min cooling 10°C/min 90mTorr	1000	25	1	[52]
2	50-200 H_2 sccm	0.06-0.23, ~10min cooling 20°C/min	1000	495 nm Cu on 5nm Ni	1	[53]

The studies of copper as the catalyst for CVD graphene are still ongoing and there is a lack of knowledge to reach an agreement on the explanation of the mechanism and kinetics of graphene formation. However, agreement has been obtained on the role

copper and nickel is playing in terms of what are the desired catalysts for CVD graphene synthesis, since copper and nickel are believed to be the most cost-effective catalysts. Drawbacks exist as well, which provides room for scientific research to reveal more mysteries on CVD synthesis of graphene.

2.2.3 Catalyst of 3-dimention graphene

2-dimentional graphene being investigated extensively, 3-dimentional graphene emerges as a new direction of graphene research. The 3-d graphene network provides a structure where graphene flakes are crosslinking and interacting with each other through Van De Waals force, which offers an advantage to be applied in energy storage application such as super capacitor application owing to its extraordinary properties originated from 2-D graphene that are highly electric conductive and high specific surface area. Those two properties are particular desired when applying in supercapacitor applications. The first article describing the synthesis of 3-D graphene was brought up by Hui-Ming Cheng's group in April, 2011 and published on Nature[54], which is called graphene foam (GF). They have come up with a template-directed CVD synthesis to grow GF by using nickel foam as the catalyst, which is shown in figure 11.

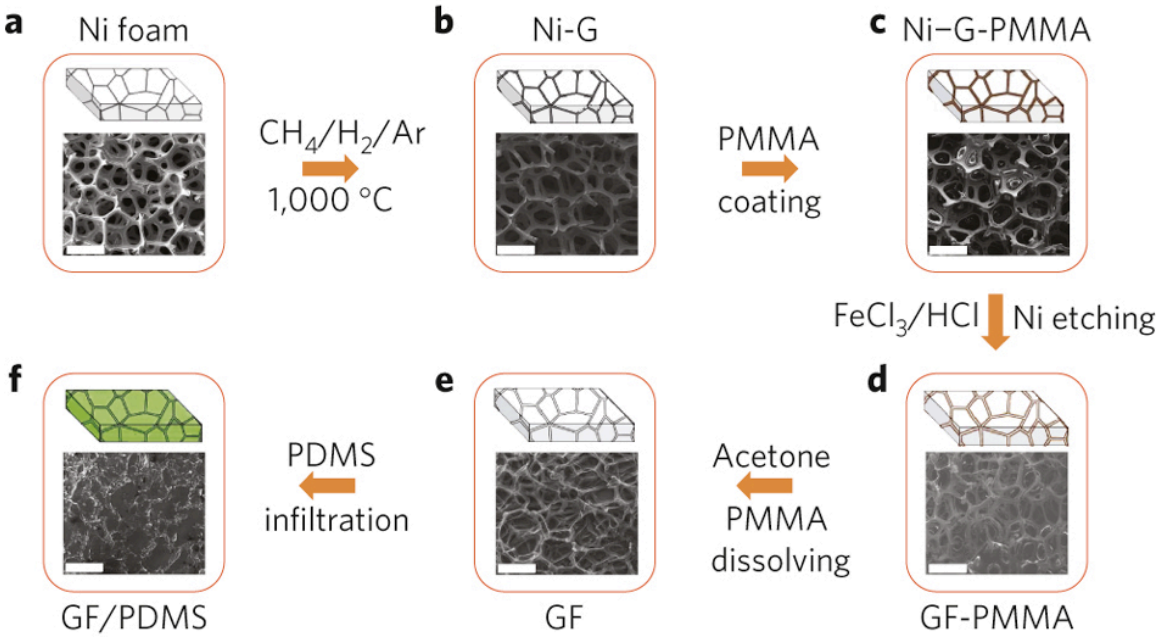


Figure 11 a,b, CVD growth of graphene films (Ni–G, b) using a nickel foam (Ni foam, a) as a 3D scaffold template. c, An as-grown graphene film after coating a thin PMMA supporting layer (Ni–G-PMMA). d, A GF coated with PMMA (GF-PMMA) after etching the nickel foam with hot HCL (or FeCl3/HCL) solution. e, A free-standing GF after dissoving the PMMA layer with acetone. f, A GF/PDMS composite after infiltration of PDMS into a GF. All the scale bars are 500 µm. Permission obtained from [54]

A series of researches in synthesizing 3-D graphene have been carried out right after the first paper published on this structure using CVD[55] and other techniques like reduce graphite oxide[7, 56]. The purpose of building 3D graphene is to taking advantage of the electrical property of intrinsic 2-D graphene as well as the super high specific surface area 3D porous graphene possessed sue to the spacing among the various orientations of graphene flakes. More studies are prevailing everyday on synthesizing 3D graphene and better properties are obtained regarding the desired performance of graphene in supercapacitor application.

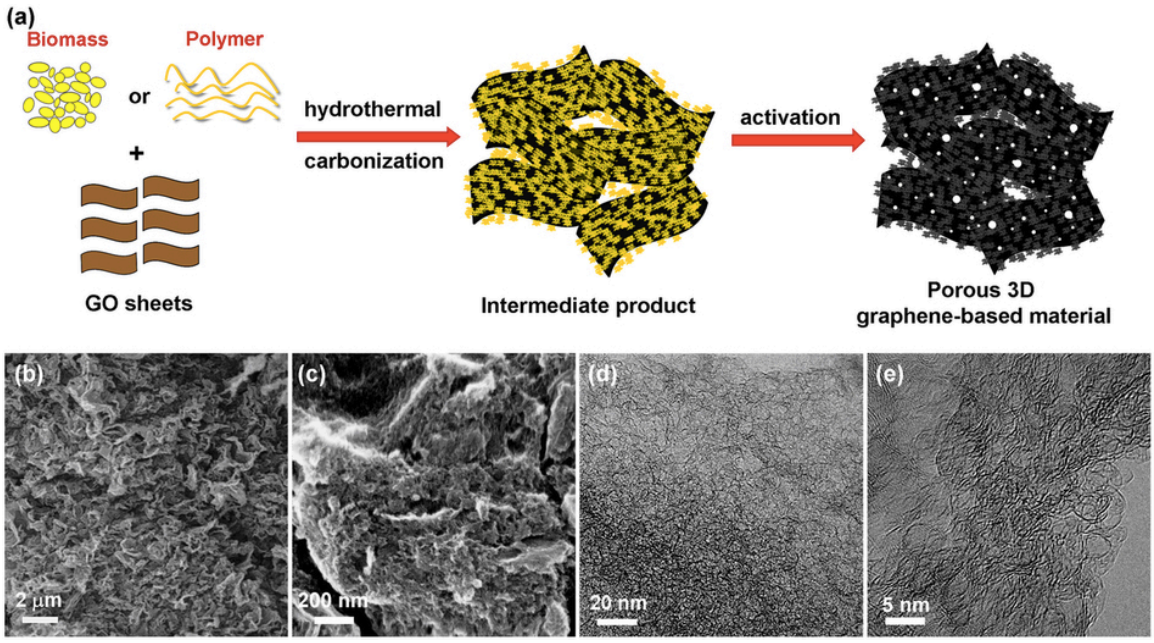


Figure 12 (a) A schematic show of the simple and green process of synthesizing porous 3D graphene-based materials.(b) Low magnification and (c) high-resolution scanning electron microscopy (SEM) images of products from the mixtures of PF and GO with optimized ratios, which exhibited sponge-like morphology and porous structure. (d) Low magnification and (e) high-resolution transmission electron microscopy (TEM) images of products from the mixture of PF and GO with optimized ratios, which also showed a dense 3D pore structure with highly curved or wrinkled surface[7].

2.2.4 Hybrid of graphene and Carbon Nanotube

Another emerging sector of synthesizing graphene related materials is to compose the hybrid of graphene and CNT, which is also mostly used in supercapacitor applications. Prior works of CVD synthesis of graphene CNTs hybrid can be classified into two categories: growing CNTs vertically on an existing graphene layer, or simultaneous growth of graphene and CNTs using CVD synthesis. Assembling vertically grow CNT arrays on an existing graphene is the more commonly adopted method; Yu Zhu, et al. with Rice University has reported a method to prepare high quality graphene with few-walled CNT carpets seamlessly connected through covalent bonds. Graphene was grown, then a film of alumina and

metal catalyst was deposited; CNTs were grown on this catalyst. The presence of covalent bonds graphene and CNT was established by STEM, and further testing demonstrated that this material has a large surface area and high electrical conductivity. Maziar Ghazinejad etc[57]. with University of California, Riverside has reported a one-step CVD synthesis, with simultaneous growth of graphene and vertical CNTs. Catalyst for CNT synthesis was deposited on copper foil (the catalyst for graphene) by e-beam deposition; LPCVD (low pressure CVD) was carried out to complete graphene-CNT hybrid growth. The resulting material had a cohesive structure with seamless contact between materials, as confirmed by TEM. Besides the CVD methods, there are other chemical and mechanical methods to assemble the composite[58-63].

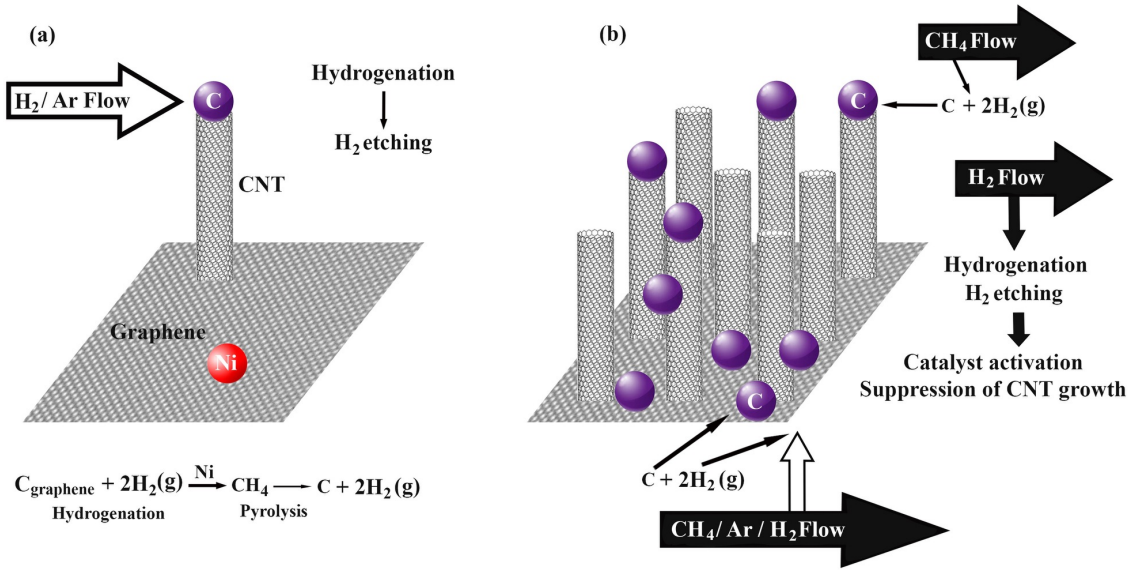


Figure 13 Schematics illustrating direct CNT growth on planar graphene (a) without carbon (methane) feedstock gas; here graphene is consumed and converted to methane via hydrogenation using Ni nanoparticles as catalyst. (b) Growth with methane feedstock: here the pyrolysis of methane supplies carbon and hydrogen to the system[64].

The most seen hybrid structure of graphene and CNT is illustrated in figure 13; additional hybrid structure will be discussed experimental session.

2.3 Characterization techniques

Many characterization techniques have been application in characterizing graphene. Among various techniques, Raman Spectroscopy, Scanning Electron Microscopy, Transmission Electron Microscopy and Atomic Force Microscopy will be discussed in this chapter.

2.3.1 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system[65]. The basic principle of Raman is based on inelastic scattering, or known as Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared or near ultraviolet range[66]. Basically, a sample is illuminated with a laser beam; the phonons from the laser are absorbed by the sample and reemitted; frequency of the reemitted phonons being shift up and down in comparison of the original monochromatic frequency telling the information about the vibration, rotational and other low frequency transitions in molecules modes in the system. The electromagnetic radiation from the illuminated spot is collected with a lens and sent through a monochromator to obtain a Raman spectrum. There is a main concern that the spontaneous Raman scattering is normally very weak and as a result of the main difficulty of Raman spectroscopy is separating the weak inelastically scattered

light from the intense Rayleigh scattered laser light. This problem is usually solved by simply cutting off the spectral range close to the laser line where the stray light has the most influence, which is low frequency area below 100cm^{-1}, that is why the Raman spectra are usually start from above 100cm^{-1} in the wavelength.

Other than the normally used Raman Spectroscopy, there are many advanced Raman Spectroscopies such as surface-enhanced Raman, resonance Raman, tip-enhanced Raman, polarized Raman, stimulated Raman (analogous to stimulated emission), transmission Raman, spatially offset Raman, and hyper Raman.

Raman spectroscopy has been adopted to characterize carbon-based materials for its capability in distinguishing the chemical nature of carbon-carbon bonds. Naturally existing carbon materials and man-made materials like graphite, diamond, carbon nanotubes, bulky ball and graphene require particular characterization tools to tell the bonding type, sp^2 or sp^3.

In graphene, the phonon energy shift caused by laser excitation creates two main peaks in Raman spectrum known as: G (1580 cm^{-1}), a primary in-plane vibrational mode, and 2D (2690 cm^{-1}), a second-order overtone of a different in-plane vibration, D (1350 cm^{-1})[67]. The exact position of the peaks can shift due to the laser excitation energy, a 532nm laser is cited here[68].

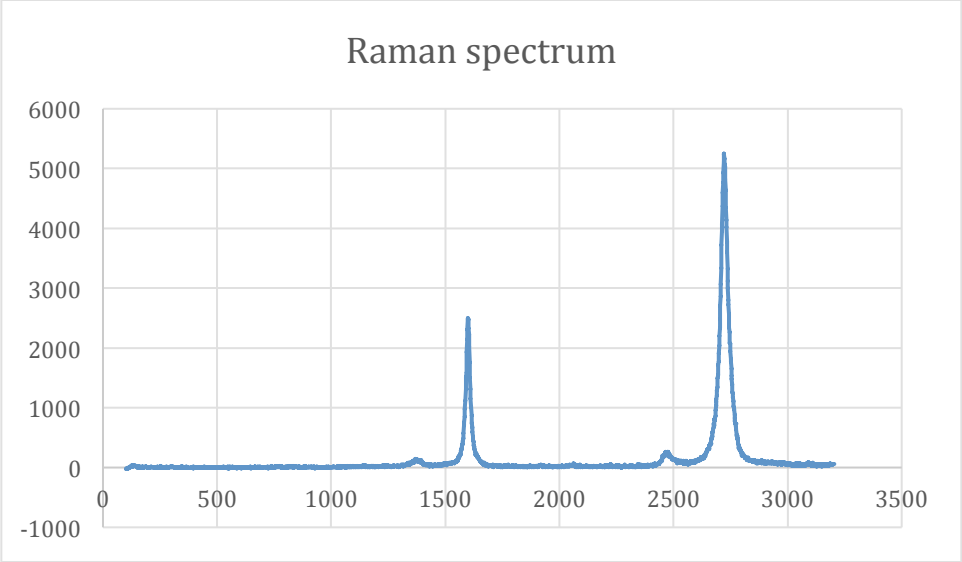


Figure 14 Raman spectrum of single-layer graphene

A Raman spectrum of single-layer graphene is shown in figure 14, where there are D peak, G peak and 2D peak. In a Raman spectrum of graphene, D peak corresponds to sp^3 bond, which is typically not desired in a Raman spectrum of graphene due to the fact that it indicates the disorder or defect in graphene; G peak corresponding to sp^2 bond, which composes graphene structure, and the geometry nature of sp^2 bond is planar triangular, which explains the 2-dimentional structure of graphene; 2D peak is always expected in a sp^2 carbon material, which is a second-order tow-phonon process and exhibits a strong frequency depends on the excitation laser energy[68]. Adding to that, the ratio between 2D and G bands can be used to obtain a rough idea of the number of layers of graphene. The reason for this is that more layers stacking adds forces from the interactions between layers of AB stacked graphene, as the number of layers increases, the spectrum will change, implicitly a splitting 2S peak into an increasing number of modes that will combine to give a wider, shorter,

higher frequency peak[69]. To summarize, the higher the ratio is of IG/I2D, the less layers are in graphene. However, Raman spectroscopy is the not the most desired technique in order to obtain the exact number of graphene layers of a sample, Atomic Force Microscopy is the best tool to characterize the accurate number of graphene layers compare to other techniques.

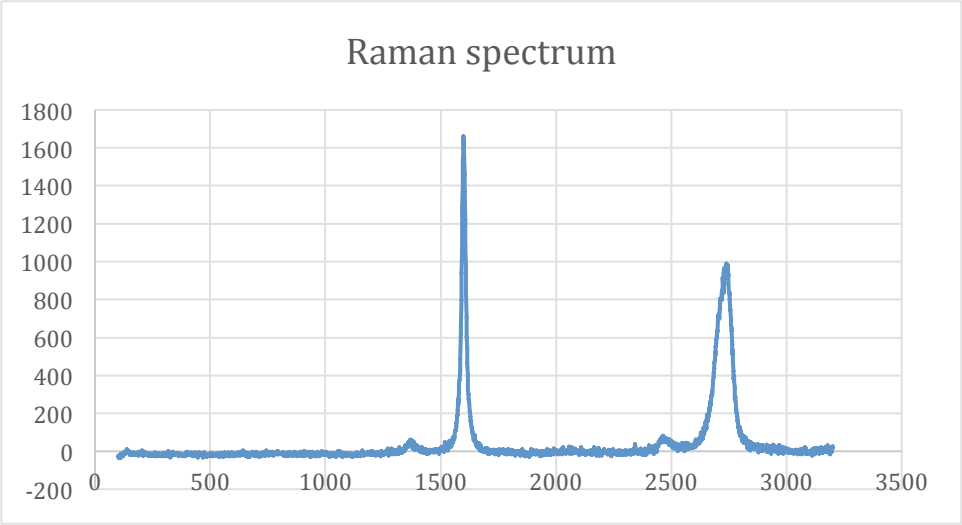


Figure 15 Raman spectrum of multi-layer graphene

It has been demonstrated that Raman Spectroscopy has high sensitivity in characterizing graphene as to the intensity; positions and shapes of the peaks will tell essential information about the quality and structure of graphene. Namely, the non-existence of D peak indicated the good quality of graphene; the ratio of the intensity of D over 2D peak supplies with the information of the rough idea about the number of graphene layers.

2.3.2 Scanning Electron Microscopy

Scanning Electron Microscopy is an imaging tool with heavy duty in the visualization of nanomaterials. It works depending on the principle of producing images of a sample by scanning it with a focused beam of electrons, where the electrons interact with the atoms in the sample, creating various signals that can be detected and that contain information about the sample's surface topography and composition. The images are produced by scanning electrons in a raster scan pattern and combining the beam's position with the signal, yielding a resolution better than 1nm in the environment like high vacuum, wet conditions, SEM can be used to visualize materials topography in nanometers range [70].

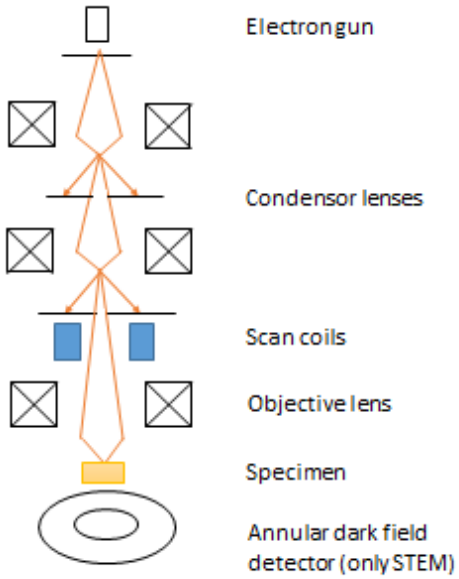


Figure 16 Lay-out of SEM set-up[71]

SEM is widely used in researching about graphene; the shape of graphene is usually confirmed by SEM before going to TEM, which can be demonstrated in figure 16.

However, there are limitations in verifying the number of layers of graphene under SEM due to the resolution limitation.

2.3.3 Transmission Electron Microscopy

The working principle of Transmission electron microscopy is that a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through, during which time the image is formed and magnified onto an imaging device, such as fluorescent screen and a layer of photographic film.

TEMs are capable of imaging at a significantly high resolution owing to the small de Broglie wavelength of electrons. TEM is frequently employed when high-resolution images are need when trying to tell the number of layers of graphene [72].

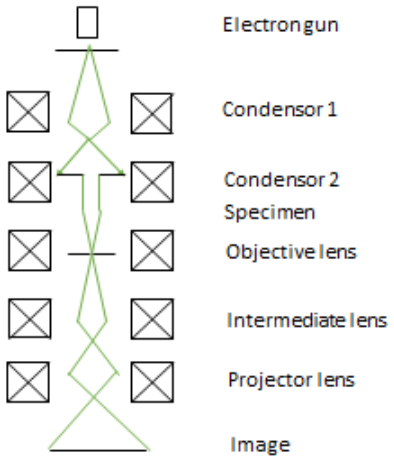


Figure 17 Layout of TEM [73]

2.3.4 Atomic Force Microscopy

The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law[74]. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces, etc.[75]. A diagram will be carried out according the force profile, giving information of the sample's morphology.

In the researches of graphene, AFM is mainly used in determining the number of layers by calculation from the information of thickness.

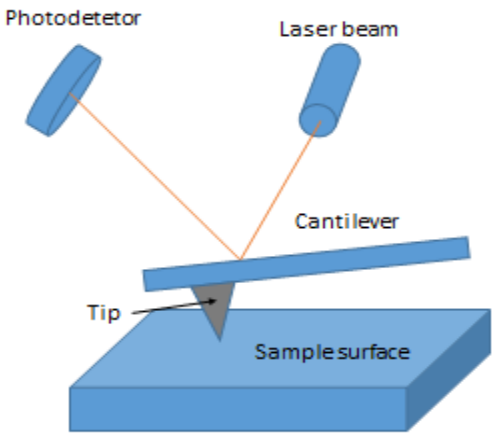


Figure 18 Layout of AFM. [76]

3. Experiment Session

3.1 Synthesize graphene use Nickel catalyst

3.1.1 Graphene synthesized on Si/SiO2 substrate coated with Ni

Chemical Vapor Deposition (CVD) is one of the most commonly used synthesis techniques for Graphene. The temperature for growing graphene could go up to 1000°C at atmosphere pressure, low pressure or high pressure, with the introduction a mixture of gases as the precursor. The set-up for CVD is illustrated in figure 19.

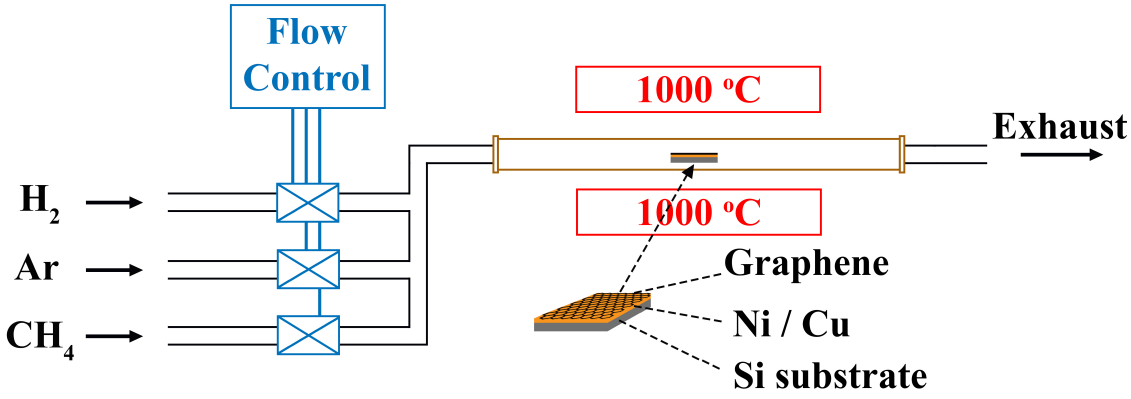


Figure 19 Schematic of CVD

Nickel is a transient metal with melting temperature of 1455°C under atmosphere. So the initiated growing temperature was 1000°C with the mixed gases of argon, hydrogen and methane. Argon was served as the buffer gas, which created an inert environment, hydrogen helped in the annealing process, and methane was served as the carbon sources. For using nickel as the catalyst for synthesis graphene, different parameters used will yield graphene with different number of layers and different

quality. The carbon atoms solubility on nickel is 0.6% weight around melting point compared to copper, which is 0.008% weight around its melting point.[77] Thus, it is reasonable to expect more layers of graphene on nickel and less layers graphene on copper. When varying the time and amount of methane serving of actual growth, it has been discovered that the less methane used, the less layers obtained, and the actual growth time can be down to 10 seconds[78]. The mechanism behind this is that carbon atoms decompose from methane onto nickel surface and some of the excess carbon atoms will dissolved into nickel surface with increasing carbon concentration over time, then carbon atoms will migrate from within nickel to the surface of nickel and start to build up more and more layers of graphene. Due to high solubility of carbon atoms in nickel, multi-layer graphene is expected from nickel, which makes it difficult to control the exact number of layers of graphene. There is another way to control the amount of carbon flowing over nickel catalyst is to use filler set-up while running CVD, this involves work of corrugated graphene and CNT arrays composite, which will be mentioned in later part of this thesis in.

Raman spectroscopy was used to confirm the existing and quality of graphene synthesized under CVD. Raman spectroscopy is the most commonly used technique to characterize carbon materials, including Florence 0D, Carbon Nanotube 1D, Graphene 2D and Graphite or Diamond 3D.[79-81] Graphene ideally is made from all sp^2 bonds. Raman spectrums have two typical feathers for sp^2 bonds, one is associated with the longitudinal optical phone mode, occurring around 1580 cm^{-1} and is called the G band; the other one is an especially intense second order dispersive Raman feature called the 2D band occurring around 2700cm^{-1}.[82] First

of all, an experiment following the recipe in table 2 was conducted, and Raman spectroscopy was used to study the existence and quality of graphene. The substrate was prepared using e-beam deposition (prepared in Clean Room) on Si/SiO_2 wafer with 200nm Ni deposition. The spectrum in Figure 23 shows three peaks, D peak, G peak and D peak. The existence of D peak means there was some defect on graphene. After analyzed the reasons for the existence of defect, several possible explanations were carried out:

(1). There could be too much carbon flowing in the system, since the ratio of the concentrations of the gases is Ar: H_2: CH_4 =1000: 325: 250 sccm, methane flow exceeded the saturation of the amount Ni can take. And two much carbon could result in some amorphous carbon trapped in between the layers of graphene, showing defects in Raman spectrums.

(2). The growth time was longer than needed, because the long the time was, the more methane flowing totally, which again could lead to excess amorphous carbon.

(3). The cleanness of the substrate surface could affect the quality of graphene, because the existing of dirt could result in unexpected chemical after CVD.

By optimizing the parameters in CVD recipe, multi-layer graphene with good quality was yielded using the recipe listed in table 2.

Table 2 Growing conditions via CVD

0-1000°C	1000sccmAr	40min	Temperature Ramp
1000°C	1000sccmAr,325sccmH_2	15min	Annealing
1000°C	1000sccmAr,325sccmH_2, 250sccmCH4	5min	Growth
Cool down	1000sccmAr		Cooling

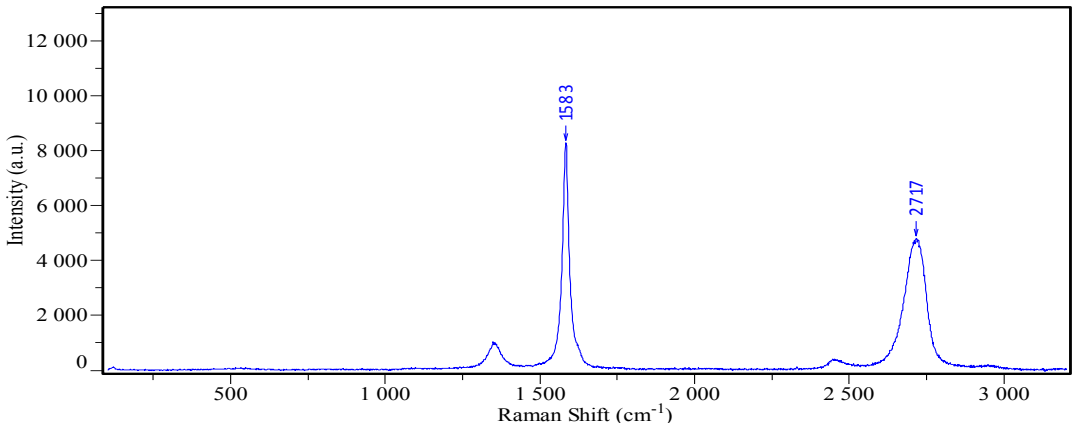


Figure 20 Raman spectrum of graphene on Ni catalyst

Optimized recipe for growing graphene on 25μm Ni foil. As for the expense concern, 25μm Ni foil (Alfar Aesear No. 40714) was chosen as the substrate for graphene instead of Si/SiO_2 wafer coated with 200nm Ni. The optimized recipe for Ni foil is listed in table 3, with reducing methane concentration, reducing growth time, and adding hydrogen in the first step with argon to initiate the inert environment in the chamber.

Table 3 Optimized recipe for graphene growing using Ni as catalyst

0-1000°C	1000sccmAr,325sccmH_2	40min	Temperature Ramp
1000°C	1000sccmAr,325sccmH_2	15min	Annealing
1000°C	1000sccmAr,325sccmH_2, 25sccmCH4	2min	Growth
Cool down	1000sccmAr		Cooling

By studying the Raman spectrum and SEM images of graphene on Ni, the existence of good quality multi-layer graphene was observed on Ni foil.

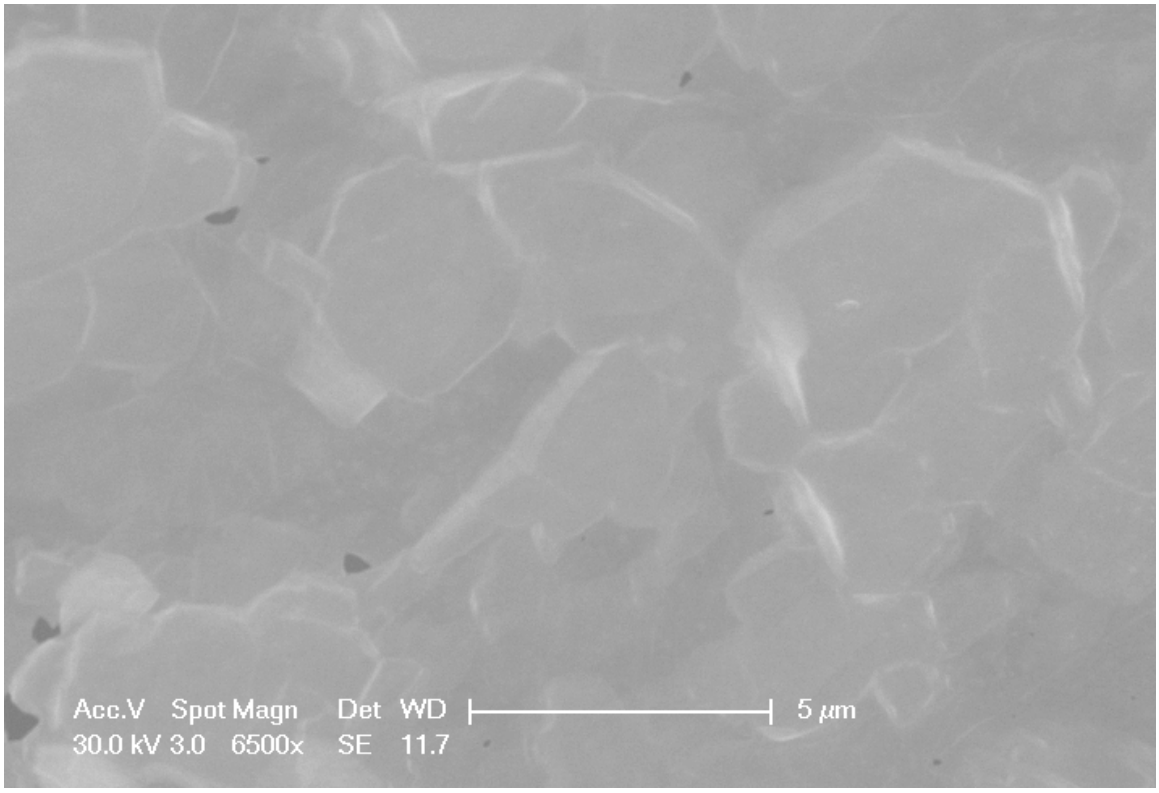


Figure 21 SEM images of Ni graphene

Figure 22 Optical image of how to design the shape of catalyst

In order to discover a way for massive produce in the future, a new design came up to make the most of the space use in the chamber. A scheme was shown in figure 22.

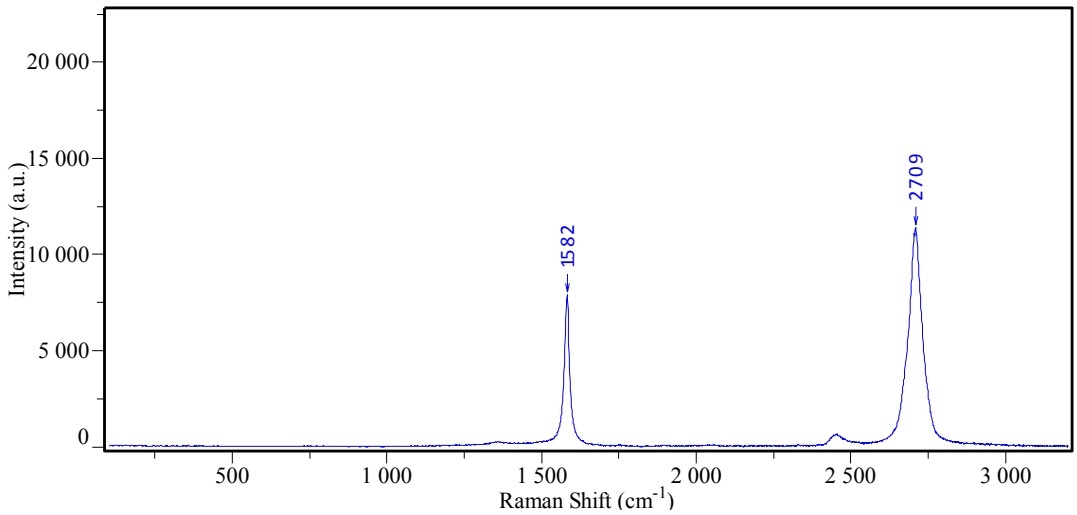


Figure 23 Raman spectrum of freestanding graphene on TEM grid.

TEM (Transmission Electron Microscope) was also conducted after transferring graphene from Ni foil to TEM grid. (Figure 24) The transfer procedure was to use nitric acid to etch away nickel and then rinsed with distill water for three times until there was no nickel left, a TEM grid made of nickel and carbon lases was used to fish out graphene flakes floating in water after rinse.

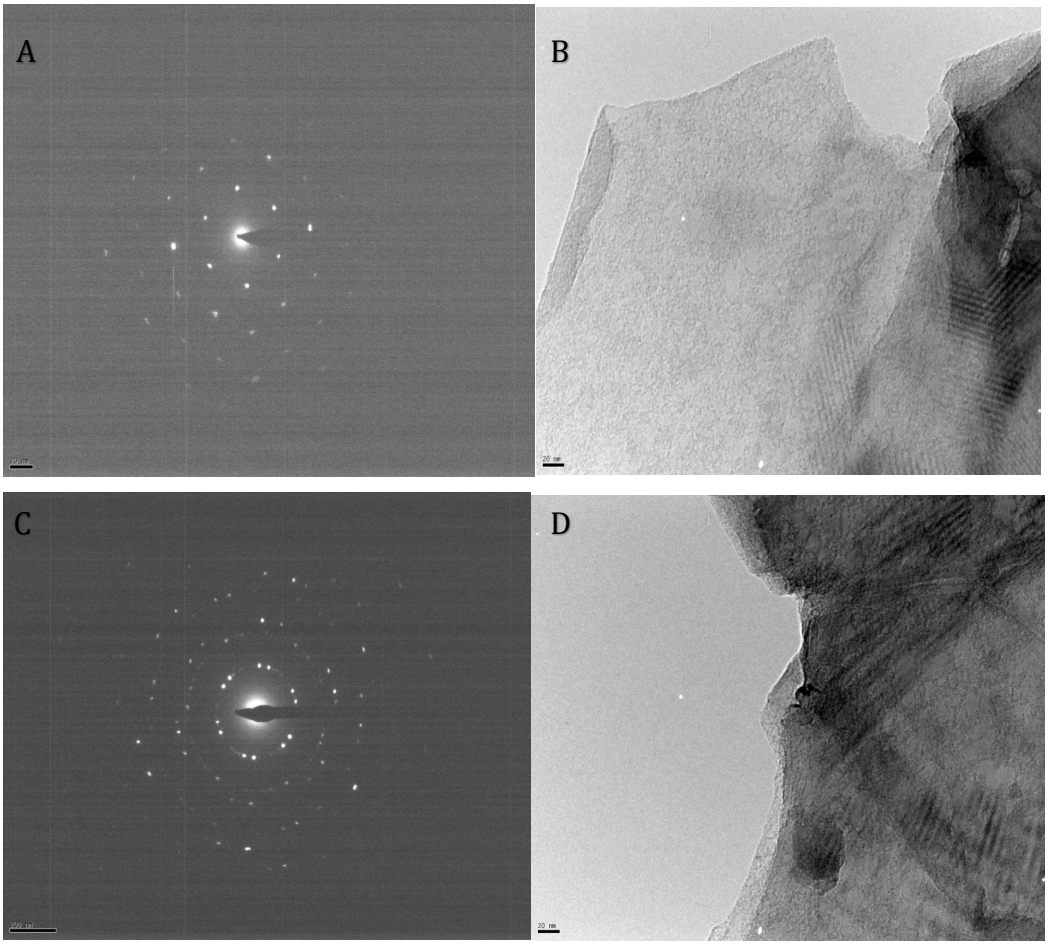


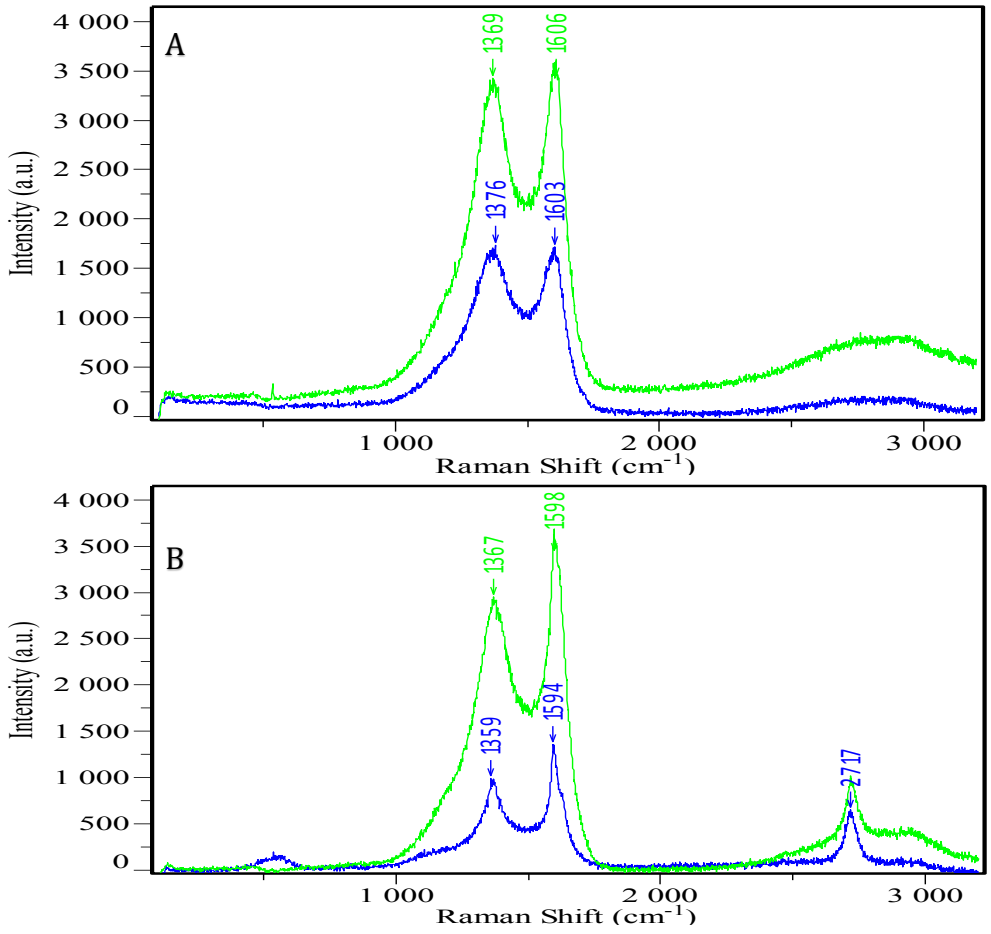
Figure 24 TEM images of graphene synthesized on Ni foil and transferred onto TEM grid. B and D are images for single and multi layer graphene respectively. A and C are the diffraction patterns of single and multi layer graphene respectively.

3.1.2 Graphene grew on mixed catalyst of nickel and gadolinium

The idea was borrowed form a patent[83], which introduces combining traditional catalysts for CNT based on transition metals such as Fe, Co, Ni with non-catalyst elements/promoters can increase CNT growth rate when matched to the appropriate deposition conditions. Some hypothesizes were carried out from the six mechanisms mentioned in the paper.

3.1.2.1 Hypothesis of graphene synthesis by adding promoter gadolinium

For the first mechanism, which is using additional layer of Lanthanides metal can lower the melting point of the resulting alloy through formation of a eutectic composition thus decreasing the growth temperature of the CNT array, reducing growth temperature for graphene with Gadolinium involved was the first hypothesis, and a series of experiments were conducted following the optimized recipe but deducted temperature by 25°C until there was no graphene.



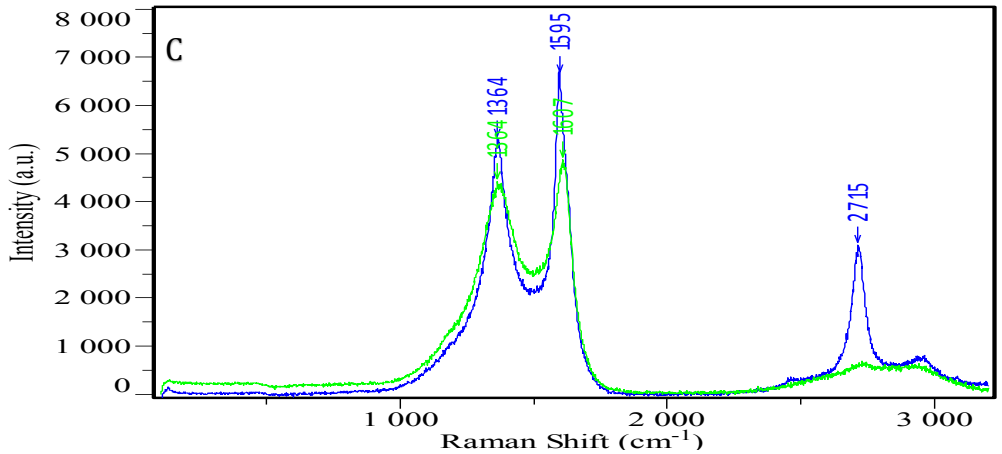


Figure 25 Raman spectrum of graphene under 975°C from the substrates respectively. A,B and C correspond to substrates 1,2 and 3.

The substrates prepared are listed below:

1. $Si/SiO_2/5nmAl_2O_3/300nmNi/100nmGd$;
2. $Si/SiO_2/5nmAl_2O_3/100nmGd/300nmNi$;
3. $Si/SiO_2/100nmGd/300nmNi$;
4. (A forth substrate was prepared as $Si/SiO_2/300nmNi$ /100nmGd, but the metal layers peeled off because the layer of Ni was too thick.)

A buffer layer of Al2O3 was deposited on silicon/silicon dioxide wafer. The function of the alumina layer was to prevent the formation of metal silicate at high temperature during the whole CVD growth process[84]. The results of the experiments on these substrates were studied by Raman spectroscopy (Figure 25 shows the Raman spectrums for substrates 1, 2, 3.)

Raman spectrums show the quality of graphene is rather poor when temperature

dropped from 1000°C to 975°C. Only 25°C lower and the formation of graphene were difficult to obtain, then the first hypothesis was broken by the Raman results.

3.1.2.2. Hypothesis of graphene synthesis by adding promoter gadolinium

A, The second mechanism explain enhancement of catalyst performance is related to digesting the excess carbon flooding the growth zone by Lanthanide element, which reduces or eliminate the risk of non-graphite contamination.

Thus, another hypothesis was carried out that reducing hydrogen flow rate would still work for graphene. Because less hydrogen flowing could give more chances for catalyst to enlarge the grain size, which is related to the graphene flake size: the bigger the grain size of the metal, the larger the graphene flake is.[85]

B, Another theory from the patent[86] was that the Fe-Lanthanides catalyst possesses the capability of extending the catalyst lifetime and maintaining constant grown rate until the growth terminates. A hypothesis about increasing the growth time might lead to more continuous and uniform graphene layer, but further experiment result showed the longer time growth, the more layer deposited.

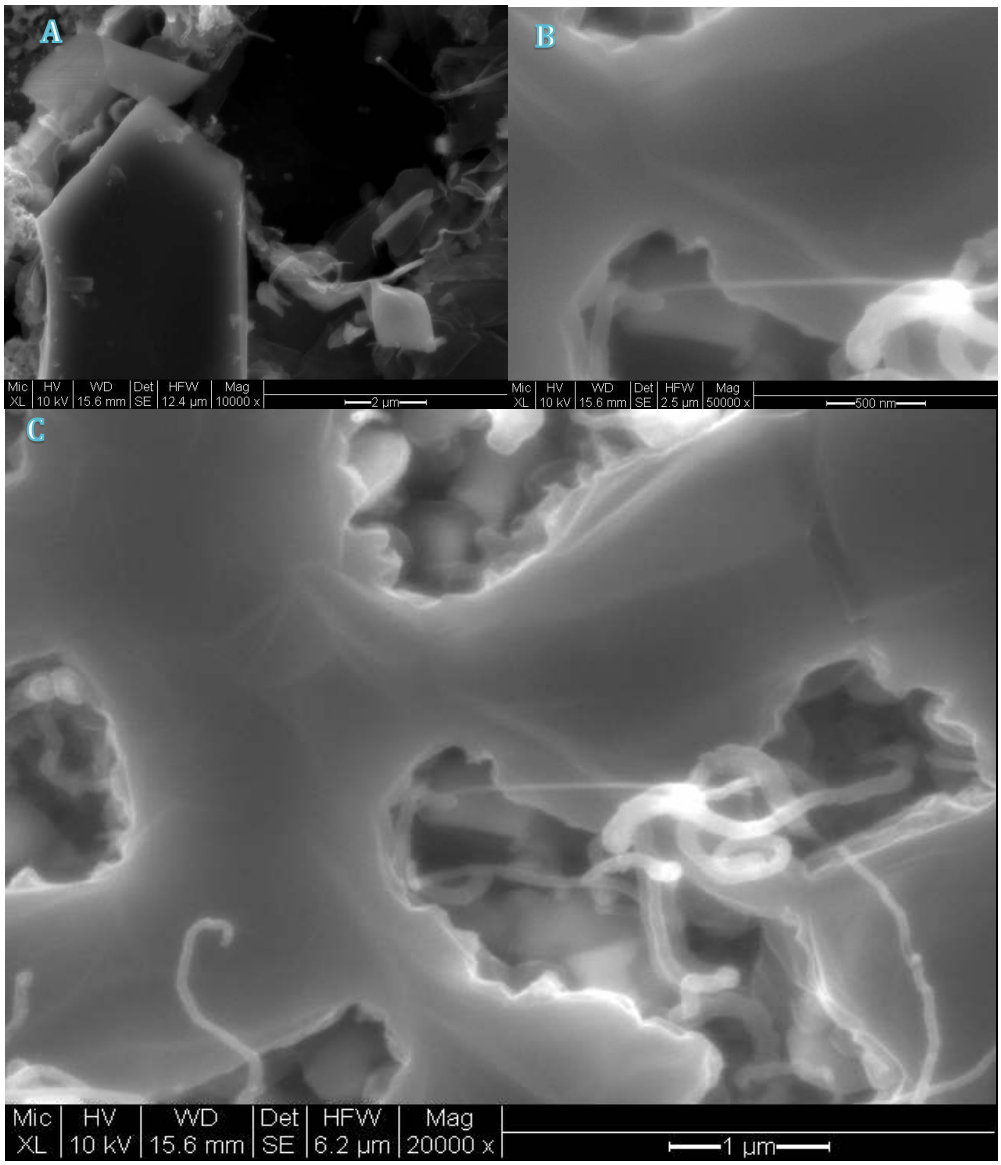


Figure 26 SEM images of sample two ($Si/SiO_2/5nmAl_2O_3/100nmGd/300Ni$) using recipe (0-1000°C: 1000sccm Ar; 40min; 1000°C: 1000sccm Ar, 325sccm H2; 15min; 1000°C: 1000sccm Ar, 325sccm H2, 250sccm CH_4; 5min).A, B and C are images with difference magnifications.

Figure 26 shows the SEM images of graphene grew on a substrate consists of Si/SiO2/5nmAl2O3/100nmGd/300nmNi. The background seems to be a continuous sheet with a lot of pores and there are also some bundles of carbon nanotubes growing. A possible explanation could be that the thin layers of nickel and gadolinium cracked at high temperature growth, carbon nanotubes started to grow upon the exposed interface of nickel and gadolinium, meanwhile, graphene grew on

the flat surface of the substrate. Thus, a hybrid of graphene and carbon nanotubes was created. Further experiment on this discovery could be to pattern the cracks of nickel and gadolinium in return, the growth of CNTs could be patterned as well, and this method could be one-step growth of building graphene and CNT hybrid.

3.1.2.3 Adding gadolinium to reduce layers grew on Ni

To figure out the exact role of gadolinium played during CVD synthesis, a series of experiments were conducted under the recipe showed in table 4, with different configurations of the substrate:

A, $Si/SiO_2/5nmAl_2O_3/300nmNi/100nmGd$;

B, $Si/SiO_2/5nmAl_2O_3/100nmGd$ /300nmNi;

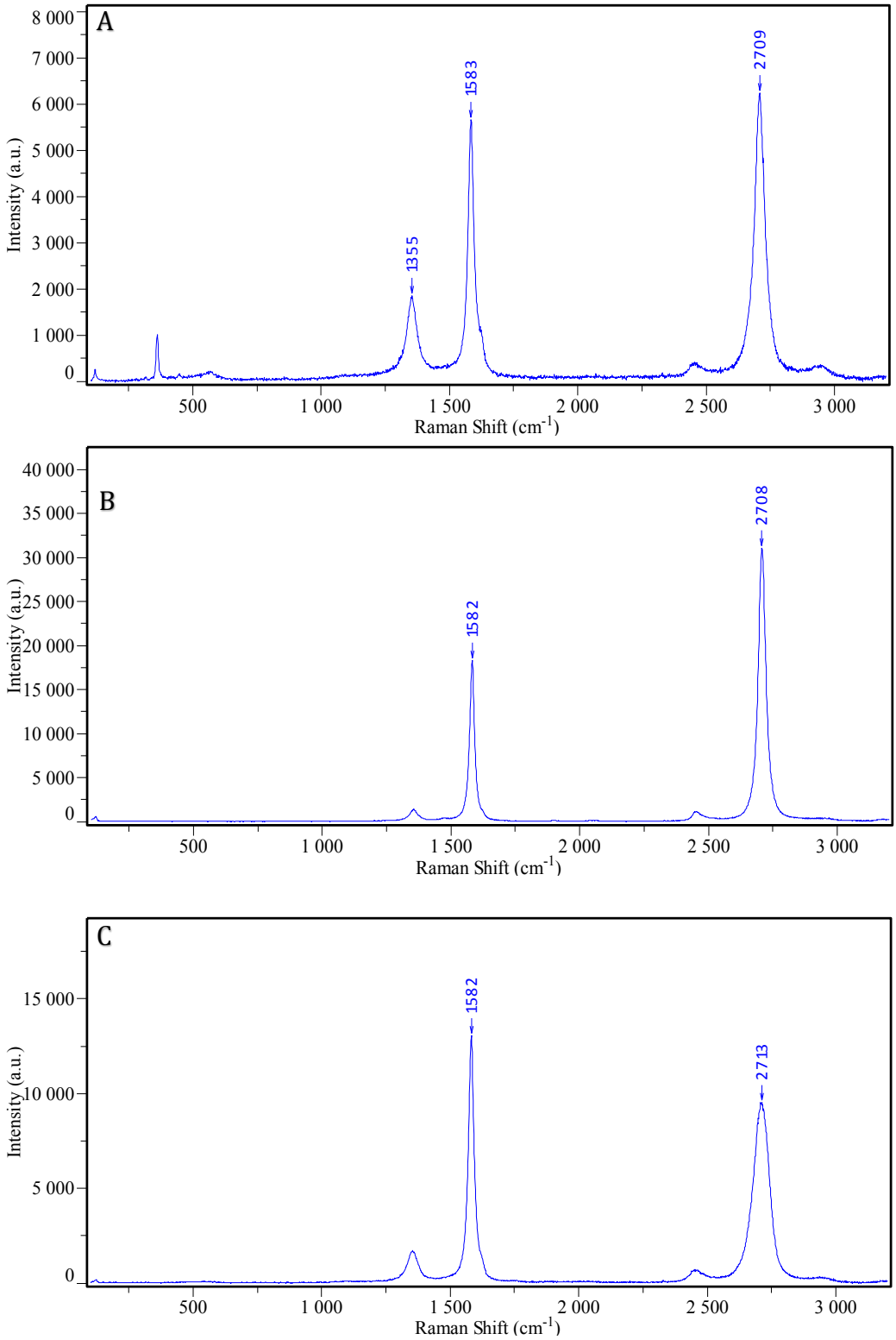
C, $Si/SiO_2/5nmAl_2O_3/200nmNi$;

D, $Si/SiO_2/200nmNi/50nmGd$;

E, $Si/SiO_2/100nmGd/300nmNi$

F, $Si/SiO_2/200nmNi$

Raman spectrums in Figure 26 show the differences of graphene grew on different substrates.


A
8 000
7 000
6 000
5 000
4 000
3 000
2 000
1 000
0
Intensity (a.u.)
1355
1583
2709
500
1 000
1 500
2 000
2 500
3 000
Raman Shift (cm-1)
B
40 000
35 000
30 000
25 000
20 000
15 000
10 000
5 000
0
Intensity (a.u.)
1582
2708
500
1 000
1 500
2 000
2 500
3 000
Raman Shift (cm-1)
C
15 000
10 000
5 000
0
Intensity (a.u.)
1582
2713
500
1 000
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2 500
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Raman Shift (cm-1)

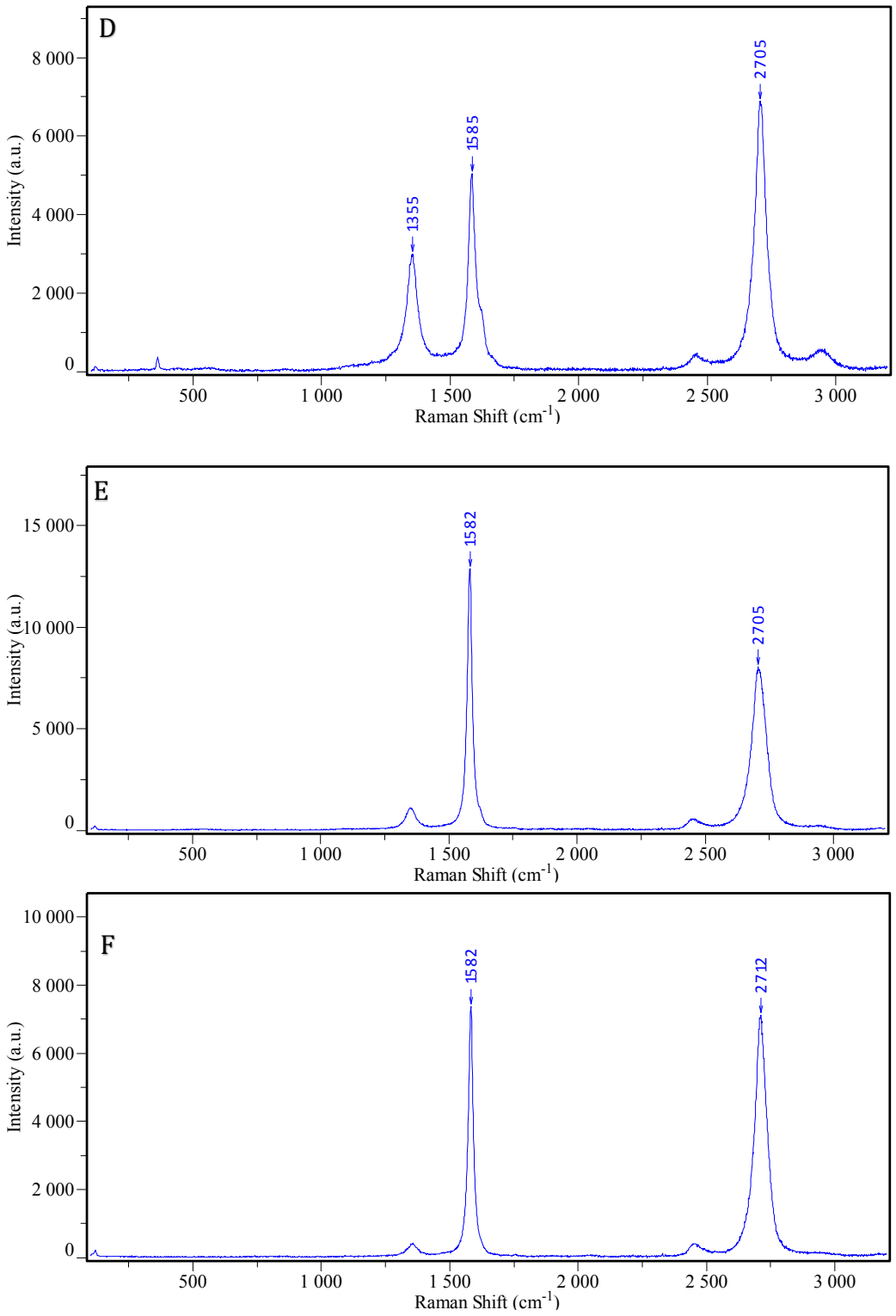


Figure 27 Raman spectrums of graphene grew on different substrate following the order A-F.

From these Raman spectrums, it can be concluded that the defects of graphene

on the substrates with Ni on top were less than the substrates with Gd on top. Moreover, Raman spectrums of substrate A, B, D, E had lower G/2D ratio, which means the number of graphene layers on these substrates that had an addition layer of gadolinium were less than the substrates that without. In conclusion, gadolinium helped to reduce the number of graphene layers grew on nickel substrate.

Another series of experiments have also been conducted with different design of the nickel and gadolinium deposit layer to gain the knowledge of the needed thickness of gadolinium layer as to assist the formation of less layer graphene on nickel catalyst. The Raman spectrums obtained for these experiments are showed in Figure 28.

Substrates preparation:

A, Si/SiO_2+200nm Ni

B, Si/SiO_2+200nm Ni+10Gd

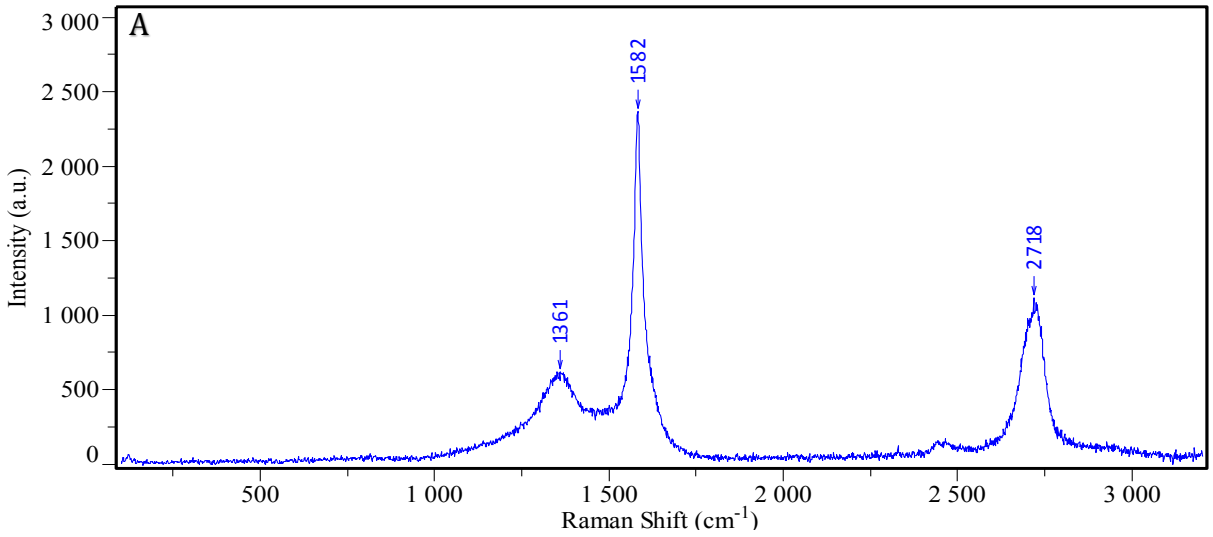
C, Si/SiO_2+200nm Ni+50Gd

D, Si/SiO_2+200nm Ni+100Gd

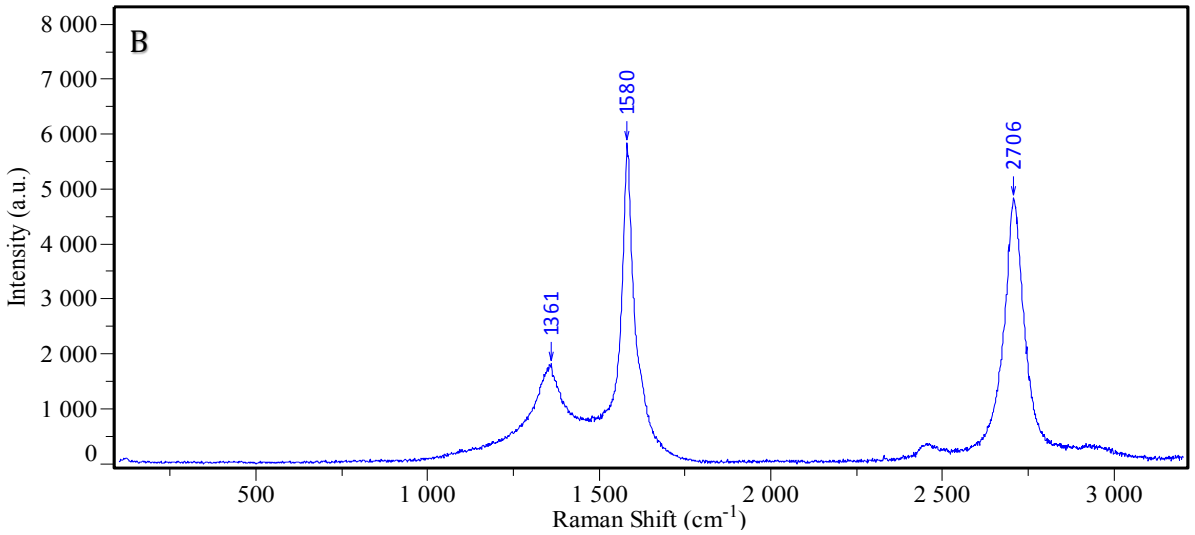
E, Si/SiO_2+100nm Gd+300Ni

Table 4 Recipe used in testing the best catalyst design by combining nickel and gadolinium

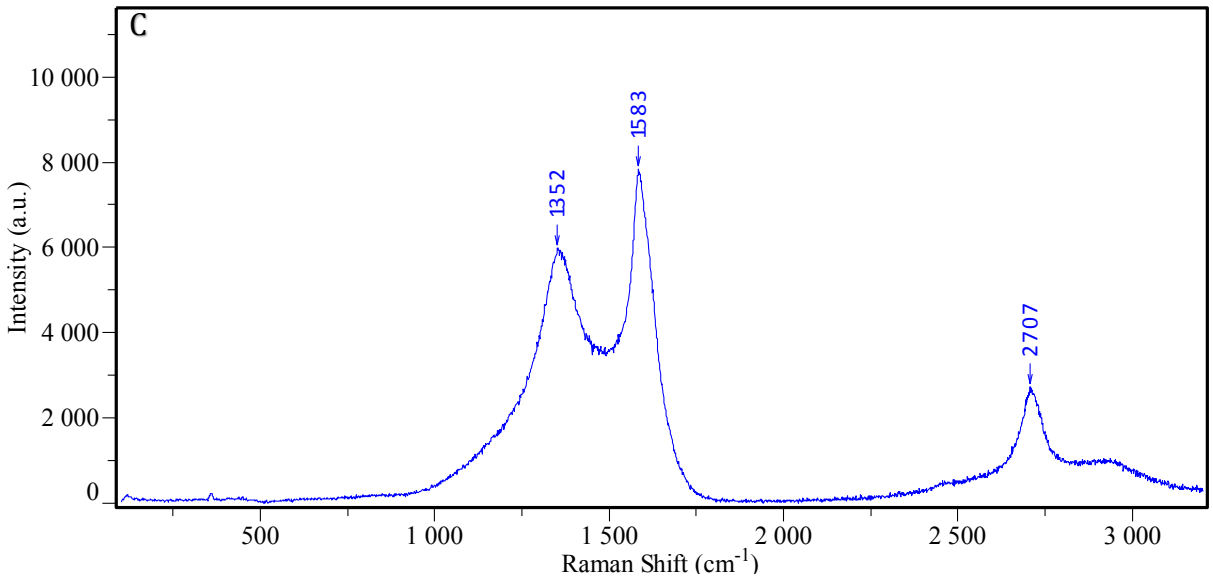
0-1000°C	1000sccmAr	40min	Temperature Ramp
1000°C	1000sccmAr,325sccmH2	15min	Annealing
1000°C	1000sccmAr,325sccmH2, 250sccmCH4	2min	Growth
Cool down			



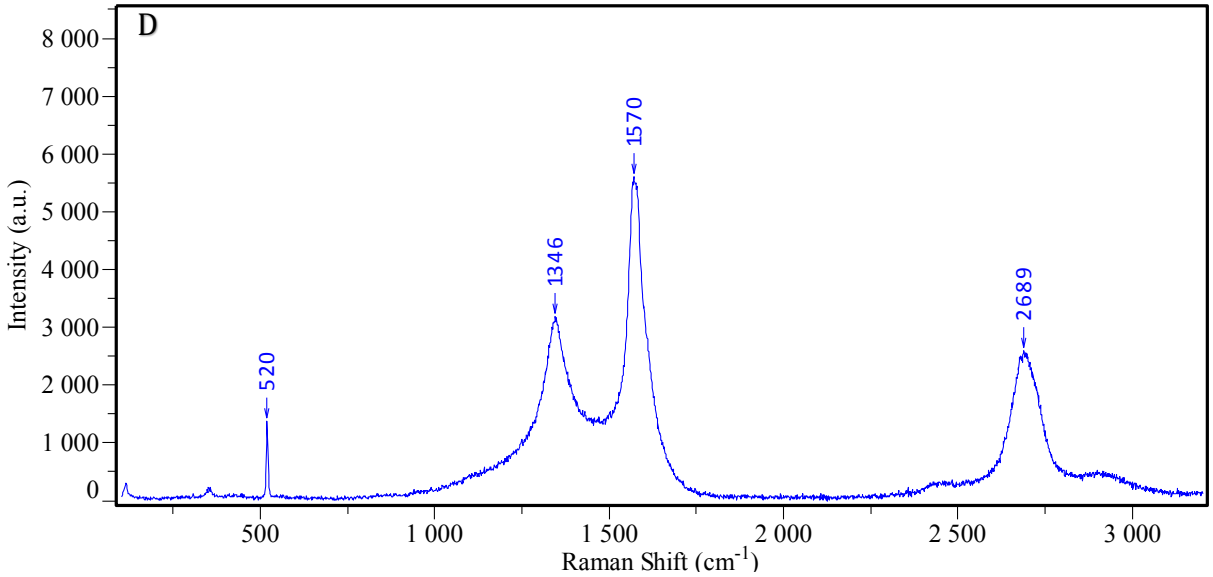
Raman spectrum of sample 1 Si/SiO2+200nmNi under 1000sccmAr_325sccmH2_250sccmCH4_2min, 2D/G ratio is 1118.86/2368.55=0.47



Raman spectrum of sample 2 Si/SiO2+200nmNi+10nmGd under 1000sccmAr_325sccmH2_250sccmCH4_2min, 2D/G ratio is 4839.59/7839.16=0.83



Raman spectrum of sample 3 Si/SiO2+200nmNi+50nmGd under 1000sccmAr_325sccmH2_250sccmCH4_2min, 2D/G ratio is 2719.49/7839.16=0.35 with D peak intensity of 5986.01



Raman spectrum of sample 4 Si/SiO2+200nmNi+100nmGd under 1000sccmAr_325sccmH2_250sccmCH4_2min, 2D/G ratio is 2591.59/5600.74=0.46 with D peak intensity of 3192.89

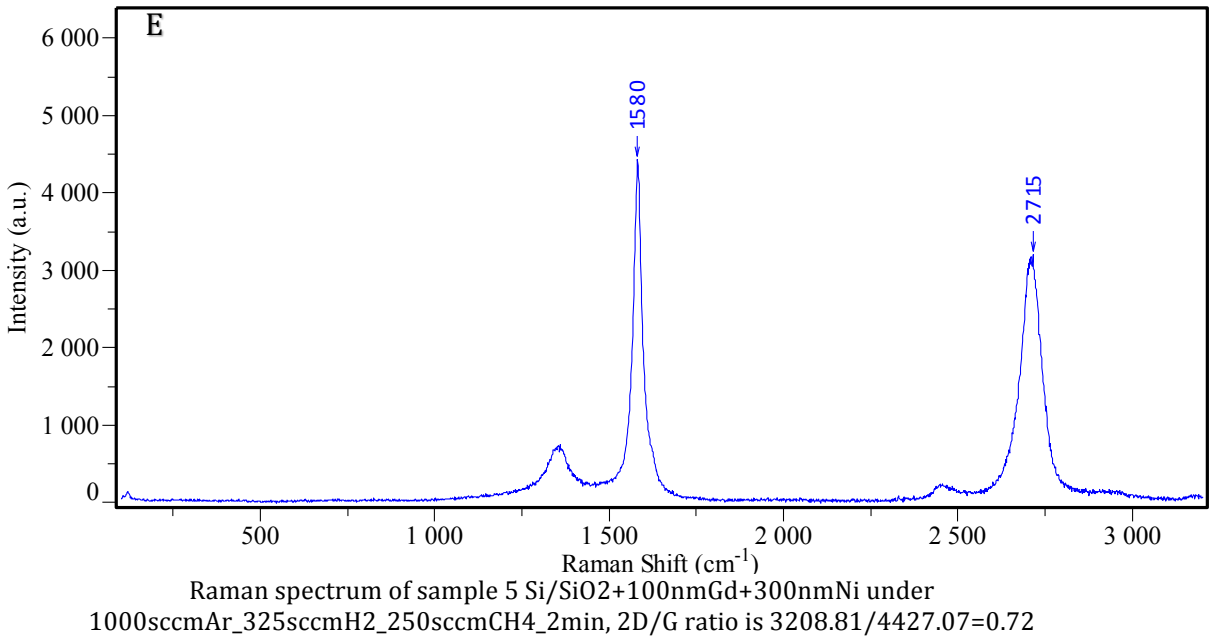


Figure 28 Raman spectrum of the substrates from A-E.

It can be concluded that with the Ni deposition on top of Gd, better results can be yielded. Sample C and D got oxidized for some reason from the optical microscope, especially the third one because it located towards the gas out side. From these observations, a conclusion can be drawn on the mechanism of adding gadolinium as a promoter for growing graphene that when the deposited layer of gadolinium and nickel was formed and placed in the CVD facility, gadolinium layer started to diffuse into nickel layer, and when carbon atoms dissolved in nickel and met gadolinium, the dissolving was depressed by gadolinium thus limited the excess layers of graphene from forming.

3.2 Synthesize graphene use Copper catalyst

Transient metals have been discovered to assist the CVD synthesis of graphene, such as nickel (discussed previously), copper and cobalt. In these methods, a mixture of

gases includes carbonic gases such as methane and ethylene are introduced in the process and heated up along with the catalyst to 1000C. These carbonic gases serve in decomposition as the carbon source as well as create the nucleation of graphene lattice formation. The formation of graphene will also be influenced by a series of other factors: the lattice structure of the metal, carbon solubility on the metal, flow rate of the gases and the thermodynamic parameters such as temperature and pressure.

As for the yielded structure of graphene, carbon solubility on the metal plays as the first role to control the number of layers of graphene, in the case of the metals have low carbon solubility, such as copper, the formation of graphene is just limited to the surface which will likely yield less layer graphene; in the case of metals have high carbon solubility, such as Ni and Co, carbon atoms will diffuse through the surface and likely form multi-layer graphene.

There are a group of impact factors for the synthesis of graphene on copper catalyst including temperature, pressure and the flatness of copper surface, which will be discussed in later part of this chapter.

When using copper as the substrate and catalyst for synthesizing graphene, copper foil is commonly used and then transferring of graphene to whatever target substrate is performed. (for example: Si, SiC, SiO_2 or bilayer graphene on aluminum to fabricate FET) Most of the deposition have been performed on copper foils with thicknesses ranging from 25~50 μm.

People have developed a graphene chemical vapor deposition (CVD) growth process on copper foils (25 μm thick). The films grow directly on the surface by a surface-

catalyzed process, and the film is predominantly graphene with <5% of the area having two- and three-layer graphene flakes.[47]

Experiments have indicated that there is little influence of deposition parameters on the physical and electrical properties of as-grown graphene on copper. However, the pre-treatment of the copper foils has been found to be important in obtaining large graphene domains in the as-deposited product. The copper substrate pre-treatment serves several important functions that ensure high quality graphene deposition. First, as received Cu is covered by native oxide (CuO, Cu_2O), which reduces its catalytic activity. Therefore prior to deposition the Cu substrate must be annealed in a hydrogen reducing atmosphere at 1000 °C. Wet chemical pre-treatment by dipping in acetic acid has also been demonstrated to partially remove Cu_2O. The annealing stage prior to deposition is also important for increasing the Cu grain size and rearranging the surface morphology (introduction of atomic steps, elimination of surface structural defects) to facilitate growth of graphene flakes. Typically the Cu foils are annealed for 30 min while shorter treatment has been reported for sub-micron Cu thin films. A systematic correlation between the homogeneity of grapheme domains and Cu grain size and crystallographic orientation has yet to be elucidated.[77]

Once the graphene/copper foil has been removed from the furnace and cooled, a polymer such as poly- dimethylsiloxane (PDMS) or polymethyl methacrylate (PMMA) can be spin- coated onto the graphene as a support, and then the copper removed using an etchant such as ferric chloride ($FeCl_3$). This leaves the graphene attached only to the polymer, which can be positioned onto any other substrate

(such as a solar cell). A solvent can easily dissolve the polymer, leaving just the graphene on any desired substrate.

Here shows the schematic diagram of the transfer process to an arbitrary substrate.[87]

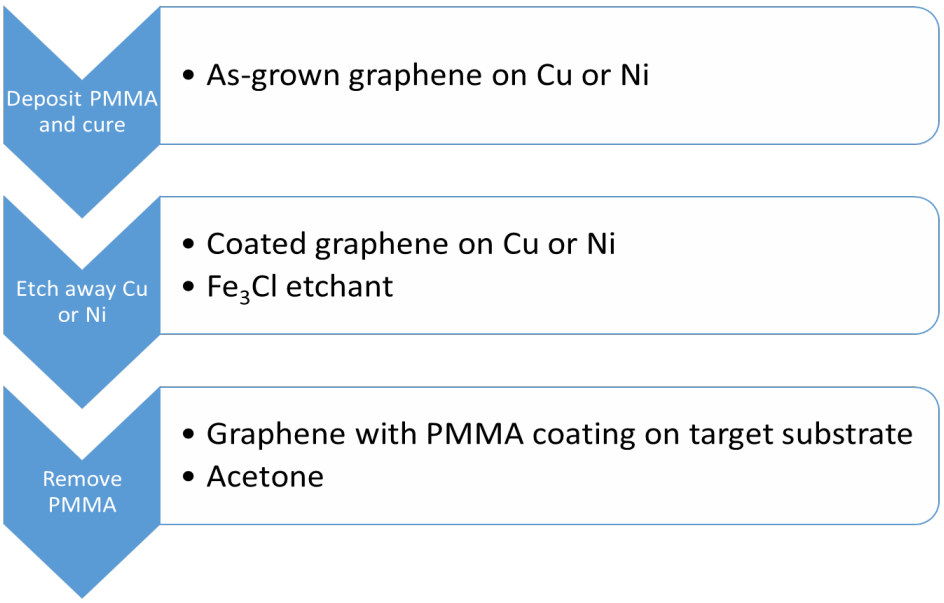


Figure 29 Transferring method of graphene.

AIXTRON's BM systems can operate in both thermal CVD and plasma-enhanced CVD modes, which is extremely important for controlling the structure of nanomaterials as it enables virtually all variations and morphologies of carbon nanotubes and graphene to be produced. The systems feature fast ramp rates, automatic recipe execution, excellent uniformity and reproducibility for nanomaterial growth. The systems are based on the highly scalable showerhead concept and are available for wafer-sizes from 50mm to 300mm diameter[88].

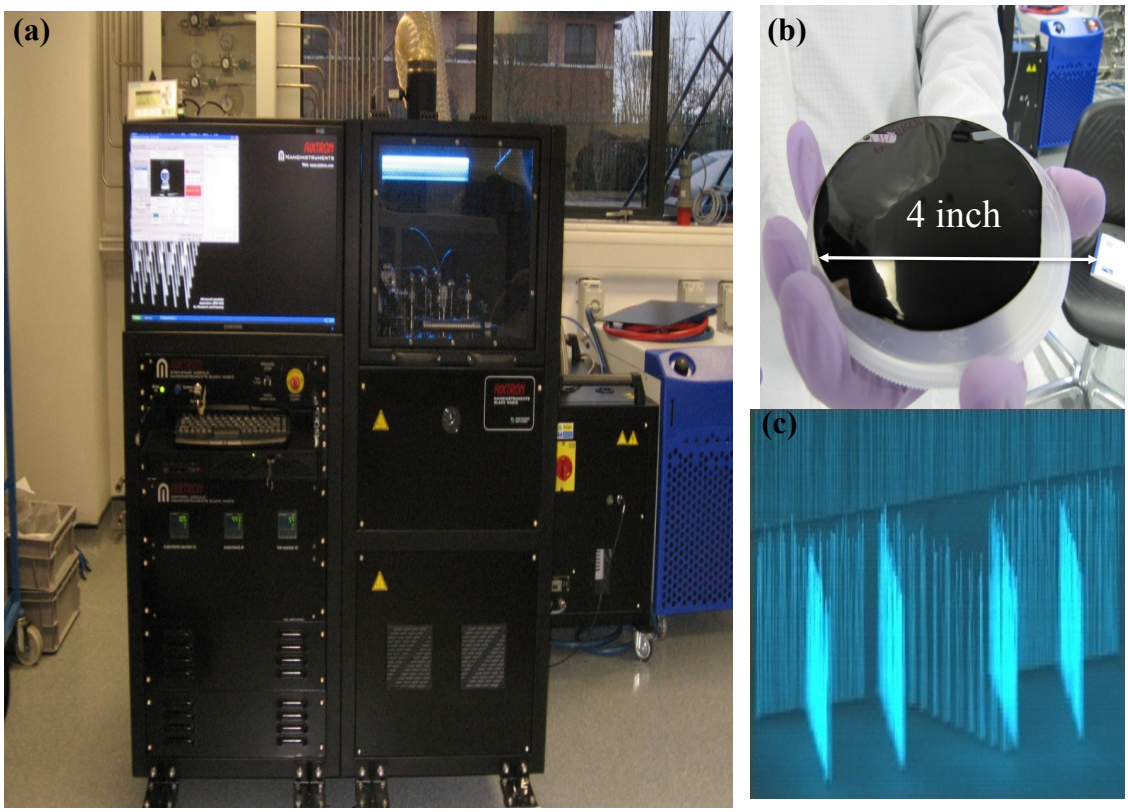


Figure 30 Black Magic module. (a); the 4-inch wafer fit in the system in (b); the side view of the CNT arrays synthesized by Black Magic in (c).

The key features of Black Magic are: 1050°C substrate heater; uniform gas delivery through showerhead; precise precursor concentration control; heater showerhead gab adjust; wafer rotation during process; ARGUS real-time wafer temperature mapping; optical ports at normal incidence to wafer.

The experiment of synthesizing graphene on copper substrate (Copper foil Alfar Aesar 46365) was carried out in the Black Magic facility.

Raman spectroscopy was employed to verify the growth of graphene, which is showed in figure 31 Raman spectrum of copper graphene. The SEM images presented in Figure 32 offer a visualization of the graphene flakes, which is

hexagonal shape. It can be concluded that the graphene flakes are intended to form along the polishing lines [89] of copper foil.

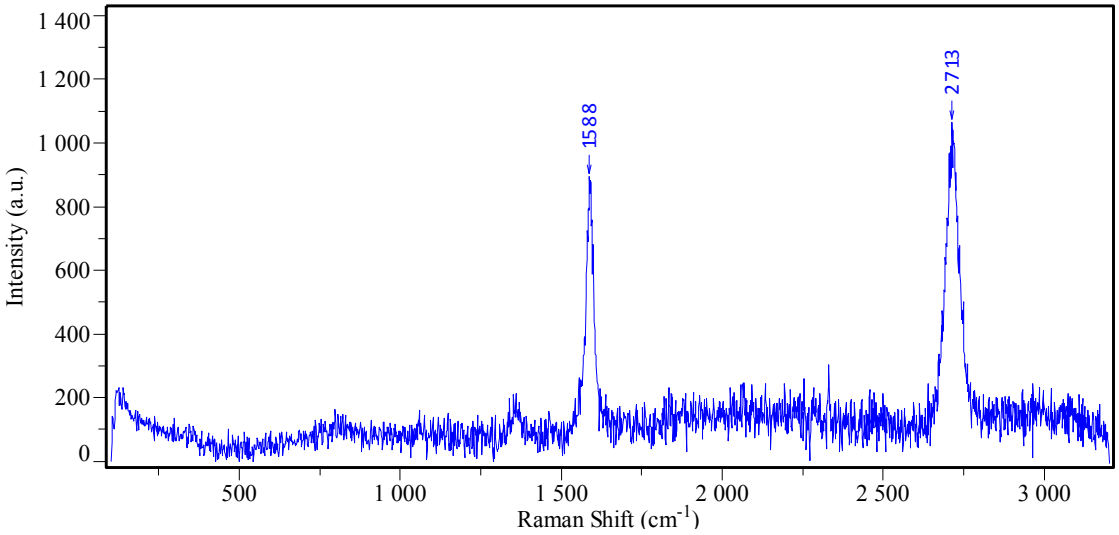


Figure 31 Raman spectrum of copper graphene

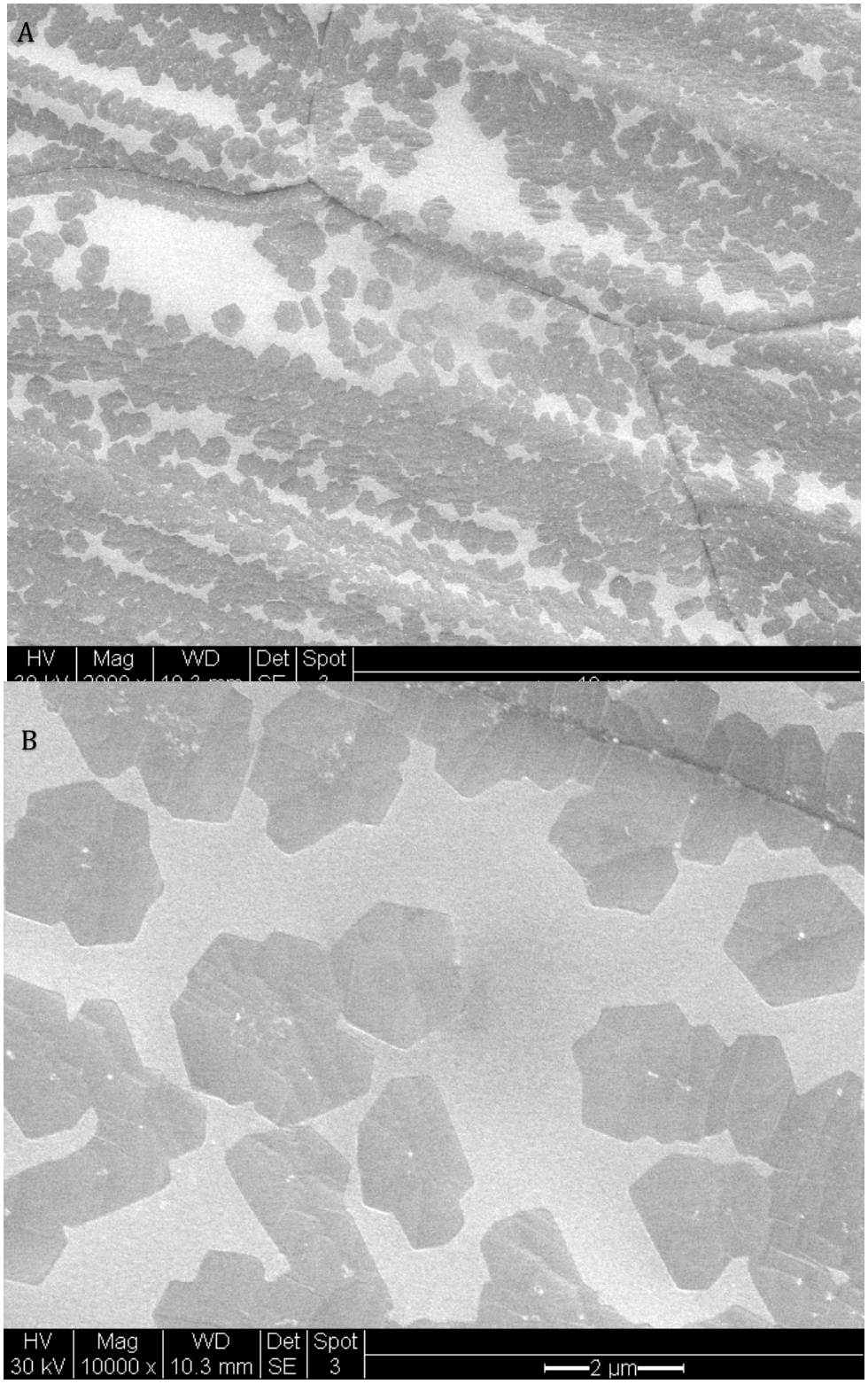


Figure 32 SEM images of graphene flakes growing on copper foil. A and B are images with difference magnifications.

The single layer graphene synthesized by Black Magic has excellent quality and it can be upscale to satisfy industry production in the future. The whole process takes 1.5 hours. After transferring graphene from copper substrate to a target substrate, graphene can be employed in applications.

3.3 Graphene and Carbon nanotube arrays composite as electrode

Research into electrode materials has expanded as the need for high efficiency electrodes in supercapacitors, sensors, and medical devices has increased. Carbon-based nanomaterials have always been a promising candidate for electrodes. Several allotropes of carbon materials, such as carbon nanotubes (CNT) and graphene, are low-density materials, a property that can be advantageous in the fabrications of portable electronics. There are several electrochemical sensors based on graphene and graphene composites for bioanalysis[90], suggesting a bright future for graphene and CNTs composites in portable medical devices.

Carbon-based materials such as activated carbon[91, 92], CNTs[93, 94] and graphene[58, 95-100] have been used extensively in supercapacitors due to their outstanding electrical and structural properties. Activated carbon is the most used material for supercapacitors, because of its large surface area and low cost. However, the large quantity of micropores presents the electrolyte from accessing much of the carbon, reducing the mass efficiency of its electrochemical functions. Moreover, low specific capacitance per area, resulting from low electrical conductivity, limits the utility of activated carbon in high power density supercapacitor application. CNTs and graphene, with their high electrical

conductivity and large specific surface area, are good candidates for supercapacitor applications. However, single-wall CNTs are very likely to stack in bundles in which only the outmost portion participates in ion adsorption, leading to low specific capacitance. Similarly, pristine graphene is likely to agglomerate due to Van der Waals force during post-synthesis processing, producing pores that are too small for ions to enter, resulting in low specific capacitance.

Given that both graphene and CNTs have desirable properties in supercapacitor application, but they also have limitations in performing high specific capacitance. A hybrid of graphene and CNTs may be able to overcome these limitations for energy storage application. Theoretical studies have shown that the excellent properties of graphene, such as electrical conductivity and large surface area, can be extended to three-dimensions[101]. One of the best ways to extend graphene to three dimensions is to covalently bond graphene with CNTs, creating a new hybrid carbon material with the advantages of both allotropes without sacrificing any of the desired properties.

Since graphene and CNTs grow best under different conditions, it is not easy to assemble this hypothesized three-dimensional structure. Prior works have been demonstrated in 2.2.4 earlier.

Here a method to fabricate a new 3-D structure is reported, which looks like mushroom gills (Figure 33). This new structure could yield better electrode performance in applications such as supercapacitors in portable medical devices. A two-step synthesis was conducted to make a graphene/CNT array composite structure, which included a CVD growth followed by a post treatment to prepare an electrode made of the synthesized composite. The created

composite electrode was compared with commercial glassy carbon electrode to evaluate and compare the performance.

3.3.1 Experiment to synthesize CGCC

CNT arrays were synthesized in Nanoworld Laboratory, University of Cincinnati, using Chemical Vapor Deposition, and were then removed from catalyst substrate. The corrugated graphene/CNT-array composite (CGCC) was assembled during the synthesis of graphene on Ni foil; the freestanding CNT array was attached to the Ni foil. A post treatment was conducted to generate the CGCC structure; the steps are illustrated in Figure 33. A piece of freestanding CNT arrays was placed on a piece of Nickel foil on their roots, then graphene grew following the recipe of 1000 sccm Ar, 325 sccm H_2 and 25 sccm CH_4 flowing under 1000°C, and deposited at the interlayer of CNT arrays and Ni foil, the foil was etched out by HNO_3 acid. During the post-treatment (drying followed by rinsing with DI water) the CNT arrays started to densify and the graphene flakes self-assembled into the final, corrugated form. The corrugation was caused by the dragging force originating from the shrinking CNT array. This force caused the graphene flakes to stand up vertically on the tips of the tubes thus forming the "mushroom gill" like structure Figure 35 shows the top view and side view of the structure. Raman microscopy was conducted to confirm the presence and quality of graphene (Figure 36). Surface morphology was studied by SEM.

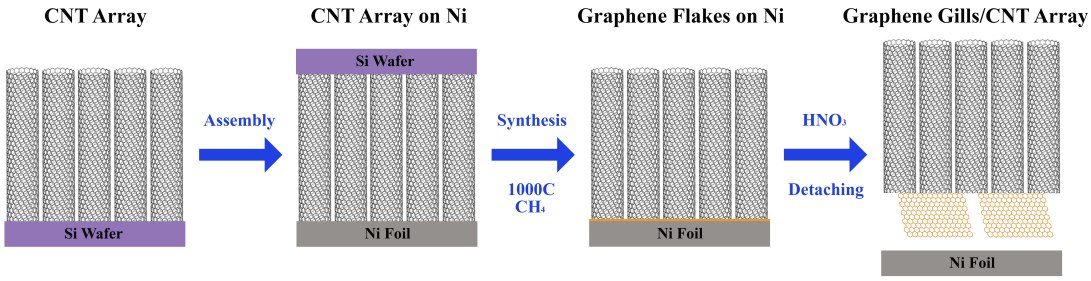


Figure 33 Illustration of the process steps to form graphene gills assembled on CNT arrays

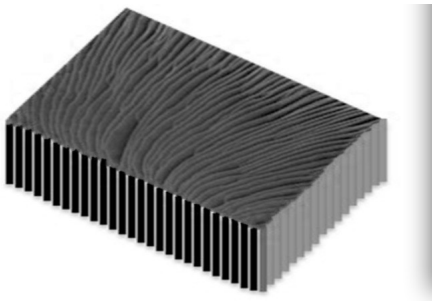


Figure 34 The ideal look of CGCC with all graphene sheets vertically assembled on CNT and aligned with each other

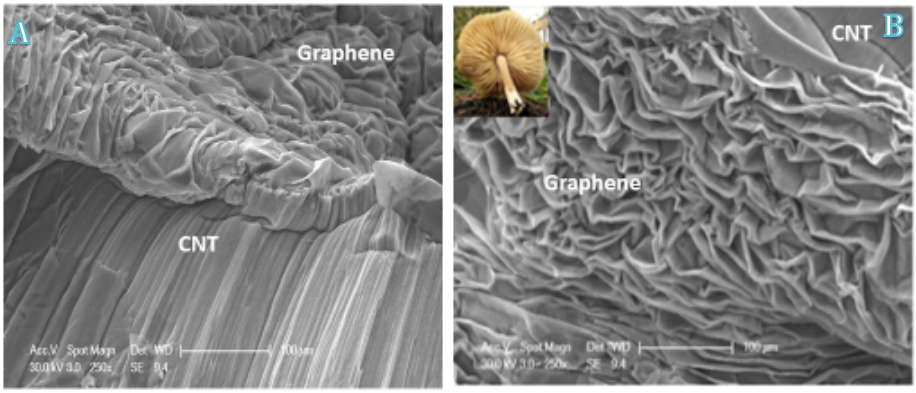


Figure 35 SEM images of CGCC. (a) The side view of CGCC that shows the vertically assembled graphene sheets on tips of CNT arrays (b) is the top view of

The electrode was made by coating a commercial glassy carbon electrode with a CGCC and Nafion mixed-paste. First, ultra-sonication was used to break CGCC into pieces in a mixed solvent of ethanol and H_2O (2:1). Then, Nafion was added to make a paste. The paste was coated (3mg) on glassy carbon electrode and was allowed to dry. A glassy carbon electrode was selected and used for comparison. The electrochemical tests were carried out in 50μM $K_3Fe(CN)_6$ aqueous electrolyte solution. The electrochemical cell employed has a three-electrode configuration. It consisted of CGCC coated glassy carbon as working electrode, Ag/AgCl (filled with 3 M KCl) as reference electrode and platinum wire auxiliary electrode. A 0.1 M acetate buffer (4pH 4.5) was used as supporting electrolyte unless otherwise stated. A three-electrode system was used in a Gamry Electrochemical Instrument, consisting of platinum as the counter electrode and as the reference electrode and the CGCC/ glassy carbon as working electrodes.

3.2.3 Result

Raman spectroscopy has been conducted on CGCC and pristine graphene grown under the same conditions. The quality of graphene can be obtained from the Raman spectrum; by calculating the ratio between G and 2D peak [69, 80], it was possible to determine that the number of graphene layers in the CGCC was less than the one for pristine graphene grown on Ni foil catalyst. As carbon atoms have much higher solubility in Ni than in copper [102]—another commonly used catalyst for CVD graphene—, multi-layer graphene was expected from Ni foil catalyst. However

during the synthesis process of CGCC, excess carbon has been limited due to the diffusion through the CNT arrays sitting on top of Ni foil.

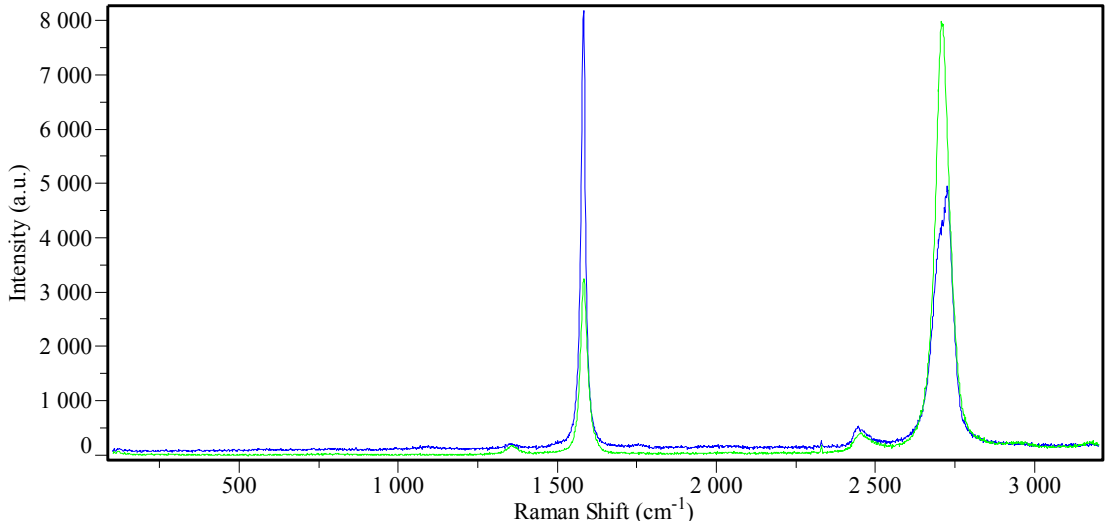
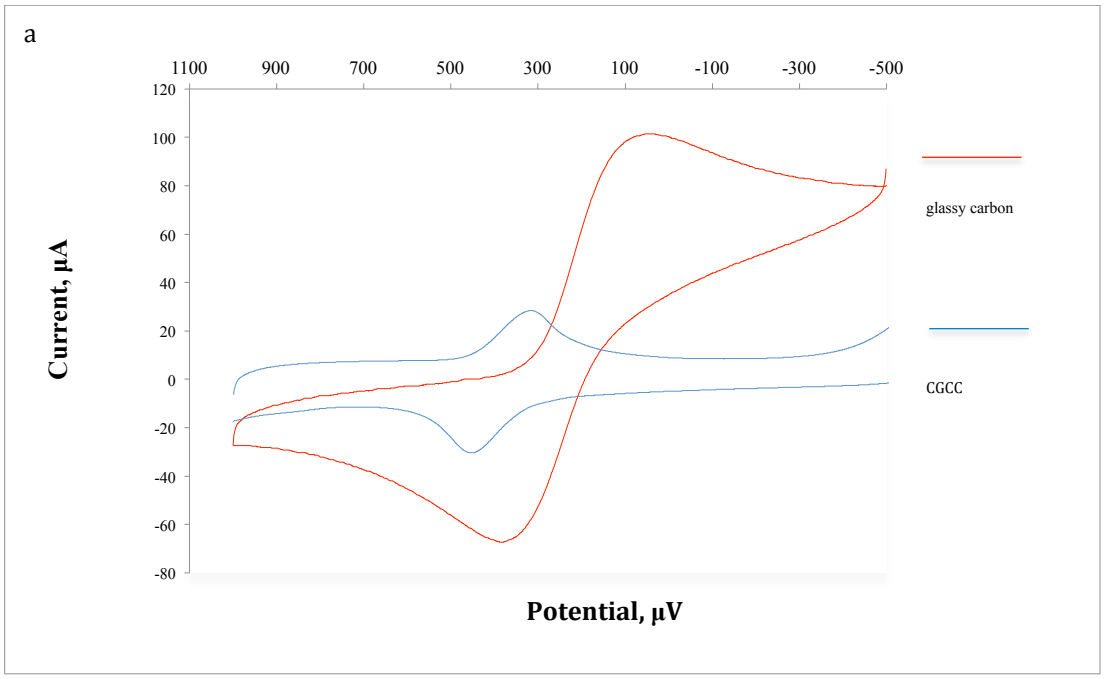
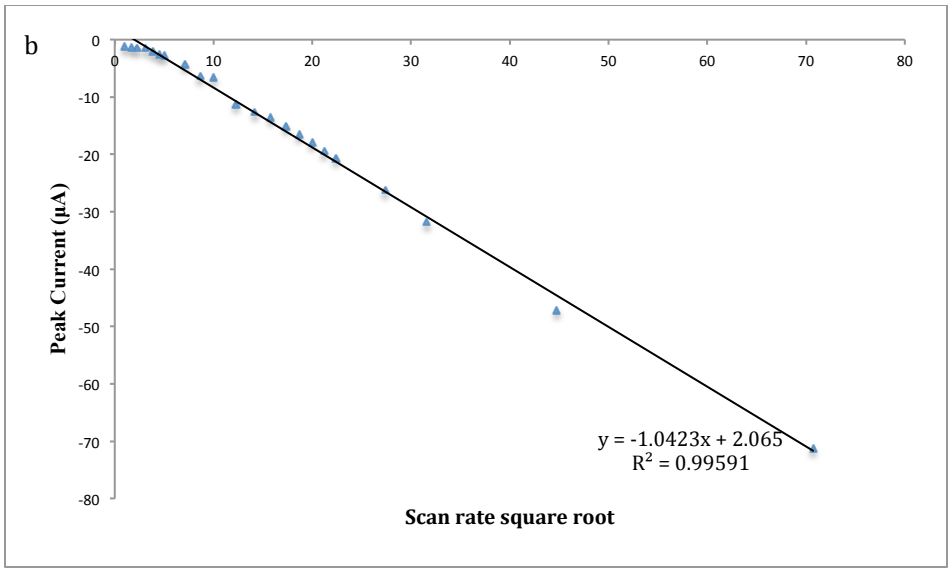


Figure 36 Raman spectrum of graphene synthesized on Ni foil and CGCC

Morphology of CGCC was investigated by Scanning Electron Microscopy. The overall structure of CGCC is similar to the mushroom gills. It is believed the covalent bonding between CNT and graphene was generated by taking advantage of the remaining catalyst for synthesizing CNT arrays on the roots, during the CVD process for synthesis graphene, CNTs continued to grow shortly at the same time graphene started to structure up. We speculate that covalent bonding exists between the graphene and the CNTs. Fig. 35 shows the SEM images of the bonded graphene flakes and CNT arrays after the self-assembly. It can be observed that the graphene flakes stand up forming a corrugated mushroom gill-like structure. It may be thermally favorable for the graphene flakes to stack together due to the van der Waals forces between the flakes [103, 104] . This restacking may be one of the limits to the performance of this graphene structure in supercapacitors, because there it

will lead to a loss of surface area. The graphene flakes rearranging themselves from horizontal to vertical position increased the exposed surface area by reducing the overlapping of the graphene. After treatment with nitric acid[105], any amorphous carbon trapped inside CNTs was removed, increasing the specific surface area from 155m2/g to 461m2/g. The average pore size is 4nm, which is within the range of pore size that provides desirable pathways for the movement of electrolyte ions [106, 107]. (Figure37) Moreover, this structure of vertical graphene and CNT provides a straight transfer path for electrons because of the parallel assembling of graphene flakes and CNT arrays.





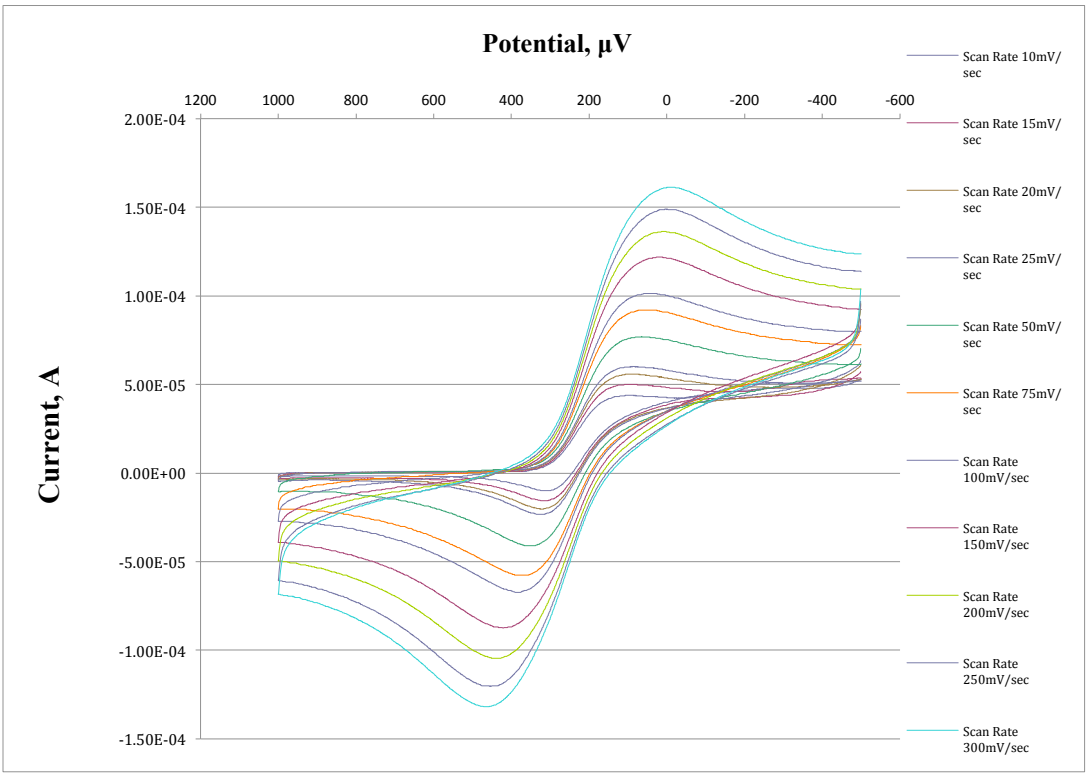


Figure 37 (a) CV curve of CGCC and commercial glassy carbon under the same scan conditions. (b) Scan rate square root VS peak current of CGCC under the scan rate from 10-5120mV/s. (c), CV curves of CGCC under the scan rate from 10-300mV/s.

Cyclic voltammetry was carried out to test the electrochemical behavior. Figure 36 shows cyclic voltammetry diagrams obtained with glassy carbon electrode and CGCC electrode in an aqueous solution under the same scan rate of 100mV/s.

There was a pair of redox waves obtained at the CGCC electrode on the CGCC with a peak-to-peak separation ΔE of 267 mV at 100mV/s (red curve in Fig. 37). This value was larger than that obtained from the glassy carbon electrode (blue curve in Fig. 40) under the same experiment conditions (68mV) suggesting that the $Fe(CN)_6^{4-/3-}$ has a slower electron transfer kinetics on CGCC electrode. This could be possibly due to the way the CGCC electrode was constructed. With the original structure of CGCC, the graphene flakes were standing on the tips of CNT arrays, which would contribute to the fast electron transferring, because the electrons could move along a carbon nanotube then jump directly to a graphene flake without switching directions. The CGCC structure was partly destroyed due to sonication and the connection between CNT arrays and graphene flakes was possibly broken. When making the paste of CGCC and Nafion, the broken pieces of CGCC may be oriented in random directions generating a network of CNTs, graphene flakes, and CNT graphene composite. This may cause limited electron transfer.

To study the mechanism of the electron transfer, a series of CV tests were carried out. At the CGCC electrode, both anodic and cathodic peak currents increase with the increase of scan rate and are linear with the square root of the scan rate in the range of 10-5120mV/s, indicating a diffusion-controlled feature of the redox process of the $Fe(CN)_6^{4-/3-}$.[108]

A new 3-D structure of graphene and CNT composite was synthesized by CVD followed by a post treatment process. This CGCC structure was used to produce an electrode and compared with a commercially available glassy carbon electrode. The performance of CGCC electrode can be improved by maintaining the structure of CGCC as embedding it to a polymer matrix. Further improvement might be realized by using single walled CNT arrays to increase the specific surface area of the composite. Future work will also include plasma functionalization of the CGCC to improve the performance of the electrode.

3.4 Future work

1. Gadolinium could be expanded to use in the synthesis of 3-dimentioanl graphene, gadolinium may have the capability to assist in synthesizing 3-dimentional graphene with singly layer flakes.
2. Graphene grew on copper foil can be transferred to arbitrate substrates and used in electronic and optical applications.
3. The structure of graphene and carbon nanotubes composite could be improved by embedding them in a polymer matrix to improve the performance eventually.

4. Application of graphene

Graphene as the emerging material in nanotechnology is provided with the possibilities to be employed in a serious of applications owing to its excellent intrinsic properties. Some of the prevalent applications such as energy harvesting, Filed-effect-transistor, sensor and drug delivery will be discussed in order to present the future of graphene.

4.1 Energy harvesting

One of the rising areas of the applications in nanotechnology is energy harvesting. It has caught people's attentions as of the possibilities of high-efficiency, very simple circuit and the fact of no memory effect in supercapacitors.[109] However, the energy density of the commercialized suoercapacitors have only achieved the value of 5–10 Wh kg $^{-1}$, which is significantly lower than the that of the lithium-ion batteries, which can reached the value of 120–170 Wh kg $^{-1}$.[110] In order to achieve a high-efficiency device, graphene and the composite of graphene have made their appearances in front of people's eyes.

There are different categories of supercapacitors in terms of the variant kinetics of storing and supplying energy; the most studied kind of suoercapacitors in using graphene if called electrical double layer capacitors (EDLC). The working mechanism of EDLCs are that they store the charge electrostatically using reversible adsorption of ions of the electrolyte onto active materials.[111] The key to make a high-efficiency EDLC by charging the double layers is to use materials with high specific surface area, where the ions are physically attached to when charging; and

high electric conductivity to speed up the physical adsorption of the ions. In this regard, graphene and the composite of graphene have their advantages due to the high electric conductivity and specific surface area graphene has. The intrinsic capacitance of single-layer graphene was reported to be ~ 21 mF cm $^{-2}$ and theoretically, supercapacitors based on graphene materials could achieve an electric double layer (EDL) capacitance of ~ 550 F g^{-1} if all the surface area can be used.[112] Nevertheless, there is still a long way to go to reach the estimation since the practical values are far below the theoretical value. There are several papers reporting difference values of energy density of the supercapacitor made of graphene and the composite of graphene using different ways of fabricating the devices. One of the best values of the energy density of EDLCs made of graphene and the composite of graphene reached more than 200 F g^{-1} in aqueous electrolyte by N-doping reduced GO sheets.[113] One of the main reasons holding back the developing of high-efficiency supercapacitor in such ways is the restacking of the graphene layers, which significantly reduces the accessible surface area for the ions and makes the electric conductivity decrease as well, which is eventually responsible for the low value of energy density can be achieved.

Tremendous efforts have been done from the scientists to try to diminish the effect of the restacking of the graphene layers. 3-dimentional graphene and the composites of graphene have been fabricated and applied in the tailoring of the structure of supercapacitors instead of conventional 2-dimentioanl graphene and the composites of graphene. There are 3-D graphene derived from reducing GO, graphene sponges, graphene aerogel and so on, as well as the composite of graphene

with other materials such as carbon nanotubes in which case the additives are playing the role of separating graphene flakes. With all the means people have come up with to solve the limitation in reaching high-efficiency, the future of fabricating supercapacitor using graphene and the composites of graphene will be encouraging.

4.2 Graphene-based Biosensors

Another exciting area of the applications graphene is in the sensor application. The mechanism of graphene-based biosensor is rooting in the electrochemistry of graphene. For instance, compared to another amazing carbon material carbon nanotube, graphene has shown discernable attractions than CNTs, which are: (1) graphene is free from the metallic impurities, whereas CNTs possess abundant metallic impurities, which in common cases such as in the application of energy storage, wouldn't be a concern, however, in the sensing of the chemicals in human bodies that are low in concentrations, can be a significant problem. In several cases, such impurities domain the electrochemistry of CNTs even as < 100 ppm levels of impurities in CNTs, thereby leading to misleading results. (2) The production of graphene in sensing applications can be cheaper than that of CNTs as the synthesis only requires graphite as the starting material, which is cheap.[4]

There have been numerous researches about the sensing application of graphene; Table 5 shows different types of enzymatic biosensor with their limit of detection and RSD.

Table 5 Various types of enzymatic electrodes made from graphene and GO. In all the cases the mode of detection is change in electrical current.

Glucose	Graphene-PPy	–	3 μM ± 0.5 μM	[114]
	Graphene/Nafion	4.21	1.0×10^{-6} M	[115]
	CVD grown graphene	–	0.1 mM	[116]
	GO	5.8	–	[117]
	PVDF-protected graphene	3.2	2–14 mM	[90]
	Graphene-CdS	5.3	0.7 mM	[118]
	CS–GR-AuNP	6	0.6 M	[119]
	Graphene	2.5	10 ± 2 μM	[120]
	CR-GO	4.3	2.0 μM	[121]
	Graphene	3.2	5 μM	[122]
NADH	IL functionalized graphene	4.2	5 μM	[123]
	Graphene	3.5	–	[124]
Hb	Fe_3O_4–graphene	1.6	0.5 μM	[125]
	Graphene	–	5.1×10^{-7} M	[36]
HRP	Graphene	4.48	1.05×10^{-7} M	[126]
	AuNP–graphene	3.6	1.0×10^{-6} M	[121]

There is a lot of room for the future research of the sensing applications of graphene. High surface area graphene prepared by CVD can be used to detect small biomolecules such as DNA, gaseous elements and heavy metal ions. Compares with CNTs, limited researches have been carried out on graphene/conducting polymer, nanocomposites and graphene/carbon based materials electrode. In the end, the mass production of single layer graphene is a major challenge that could be great benefit.

4.3 Other applications of graphene-related materials

Besides the applications of supercapacitor and sensing applications of graphene and the composites of graphene, there are also other interesting areas of applications such as the field-effect transistor (FET), solar cells and even in water filtration due to the extraordinary properties of graphene in beating its contenders that are being applied currently in every way. It would not be surprising that commercialized graphene product on market in near future.

5. Conclusion of this thesis work

1. Graphene has been successfully synthesized on different transient metals: nickel and copper use different chemical vapor deposition facilities. And the quality of graphene has been demonstrated by Raman spectroscopy, Scanning Electron Microscopy and Transmission Electron Microscopy. It also has been established that the solubility of carbon has relationship with the number of layers graphene has in CVD synthesis.
2. Experiments have been carried out on analyzing the role of gadolinium in CVD synthesis of graphene on nickel. Gadolinium helps to reduce the amount of carbon absorbed on nickel surface and thus helps to decrease the number of layer of graphene.
3. A composite of graphene and carbon nanotubes have been made into electrode material and it has been demonstrated that there is potential for improvement of the performance of this composite being used in electrode application.

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